Sampling strategy and statistical modelling of exposure

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Preface

This thesis in occupational hygiene has been worked out as a collaboration between the Department of Informatics and Mathematical Modelling (IMM), Technical University of Denmark and the National Institute of Occupational Health, Denmark (AMI) in partial fulfilment of the requirements for the Ph.D. degree at Technical University of Denmark.
The project was funded by the Danish Research Agency in cooperation with Technical University of Denmark and the National Institute of Occupational Health, Denmark (AMI).

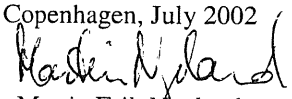
The present thesis deals with measurements of exposure to airborne chemical substances at the workplace. The thesis consists of a summary report and six articles [A – F].

Methods for estimating exposure to vapours and aerosols in the working environment are developed, proposed and applied. A method for bringing exposure under control is proposed and a system for monitoring that exposure, which has been brought under control, stays under control is proposed.

Laboratory experiments were performed at the Department of Chemical Working Environments and The Department of Indoor Climate, National Institute of Occupational Health, Denmark (AMI).

For laymen in occupational hygiene, it is recommended to read the list of glossary and abbreviations.

Copenhagen, July 2002



Martin Erik Nyeland

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First of all I wish to thank my supervisors Senior Scientist Erik Olsen, AMI and Docent Poul Thyregod, IMM, DTU. I also want to thank Senior Consultant Erik Holst, AMI. They all deserve thanks for inspiring, helpful discussions and support during this work.

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I would also like to thank the employees at the companies, involved in the present studies, for participation.

Finally I will thank Lisa and Rasmus for support and patience.

Summary

This thesis in occupational hygiene deals with air measurements of exposure to chemical substances at the workplace. The overall purpose is to estimate workers exposures at the workplace for assessing their risk for adverse health effects due to chronic exposures. Exposure and hazard form the basis of estimating and characterizing the risk, which e.g. can be done by comparing data on long-term exposures with Occupational Exposure Limits (OELs). To know the validity of the estimated exposure value, it is important to know the uncertainty of measurements and the variability of the measurement object. Exposure at the workplace is thus not a single value, but a distribution of values. When measuring exposure the intention is to estimate the long-term arithmetic mean exposure ($\bar{x}$), which can be related to risk, and its uncertainty ($\pm U$). The validity of the estimated exposure value is dependent on the sampling strategy applied (where, when and how to sample).

In the present thesis, methods for estimating exposure to vapours is exemplified by styrene, and exposure to aerosols is exemplified by ink-fly. Methods for measuring are developed, proposed and applied. A method for bringing exposure under control is proposed together with a system for monitoring that exposures, which have been brought under control, stays under control. The thesis consists of six papers [A – F] together with a summary report.

In Paper A, an improved method has been developed to determine concentrations of vapours (styrene) in the breathing zone (process concentrations) and their uncertainties (**PC** ± *U*). All uncertainty components are quantified and compared using an uncertainty budget and rules for combining uncertainties according to GUM (BIPM, 1993).

Paper B reviews the literature on particle behaviour in air and in the human airways, the sampling theory for aerosols, and sampling equipment, which currently are in use and commercial available. Decisions on suitable sampling methods for aerosol sampling can be taken based on this article.

In Paper C, the long-term average daily exposure (8h TWA) to styrene for single workers, working in a windmill wing plant, is estimated and the associated uncertainty quantified. Subsequently major

exposure sources are identified for interventions. A unique data set has been collected applying three sampling strategies. This data set allows studies to be carried out on the effect of using different sampling strategies. One of the three strategies is the new WSS[1]-logbook method, which is proposed and applied in the present thesis.

In Paper D, workers' long-term arithmetic mean exposures to 3,3'-dichlorobenzidines (in ink fly) in two heatset printing shops during a year are estimated applying the logbook method (Olsen, 1994). It is studied how results depend on the strategy applied.

In Paper E, a procedure for bringing workers exposures under control on company level, in a specific line of industry or nationwide is described and discussed. The WSS-logbook method is suggested as useful as a screening method.

In Paper F, a system is described and developed for monitoring that exposures which have been brought under control, stays under control, using adequate statistical tests.

A summary report is worked out where further detailed information is outlined on all papers included in the thesis.

[1] WSS – Workers Self Sampling, identical to SAE (Self Assessment of Exposure)

Resumé (in Danish)

Nærværende afhandling består af seks artikler [A – F] samt en rapport, der giver et samlet referat og sammendrag af artiklerne. Emnet for denne arbejdshygiejniske afhandling er luftmålinger af eksponering for kemiske stoffer på arbejdspladsen. Det overordnede formål er at estimere arbejderes eksponering på arbejdspladsen for at kunne vurdere deres risiko for sundhedsskadende effekter på grund af kronisk eksponering. Eksponering og farlighed danner baggrunden for en estimering og karakterisering af risikoen. Dette kan i praksis for eksempel gøres ved sammenligne data for langtidseksponering med grænse værdier for pågældende stof. For at kende validiteten af værdien for den estimerede eksponering, er det vigtigt at kende usikkerheden på målingerne samt variationen af måleobjektet. Eksponering på arbejdspladsen er derfor ikke en enkelt værdi, men en fordeling af værdier. Når man måler eksponering er det hensigten at estimere den gennemsnitlige, aritmetiske langtidseksponering ($\bar{x}$), da denne kan relateres til risikoen, og dens usikkerhed ($\pm U$). Validiteten af værdien for den estimerede eksponering er afhængig af den anvendte prøvetagningsstrategi (hvor, hvornår og hvordan prøvetagningen er foretaget).

I denne afhandling er metoder til at estimere eksponering for dampe og aerosoler, eksemplificeret ved styren og farve støv ('ink fly'). Målemetoder er udviklet, foreslået og anvendt. Desuden er metoder udviklet og foreslået, der henholdsvis går ud på at bringe eksponeringen under kontrol samt at overvåge og sikre, at eksponering, som er bragt under kontrol, fortsat er under kontrol.

I artikel A, er en forbedret metode blevet udviklet til bestemmelse af koncentrationer af dampe (styren) i indåndingszonen (den såkaldte proces koncentration) med tilhørende usikkerheder (**PC** ± *U*). Alle usikkerhedskomponenter er kvantificeret og sammenlignet ved brug af et usikkerhedsbudget og regler for kombinerede usikkerheder ifølge GUM (BIPM, 1993).

I artikel B gennemgås litteraturen om partiklers opførsel i luft og luftveje. Teorien for prøvetagning af aerosoler og kommercielt tilgængeligt prøvetagningsudstyr gennemgås. På baggrund af artiklen kan passende prøvetagningsmetoder for aerosoler udvælges.

I artikel C er den gennemsnitlige daglige langtidseksponering (8h TWA) for styren for enkelte arbejdere, der arbejder med produktion af vindmøllevinger, estimeret, sammen med den tilhørende

usikkerhed, som blandt andet er afhængig af den anvendte prøvetagningsstrategi. Derefter er de største eksponeringskilder identificeret til brug for intervention. Et unikt data sæt er indsamlet ved anvendelse af tre forskellige prøvetagningsstrategier. Med dette data sæt er det muligt at undersøge og sammenligne prøvetagningsstrategierne og deres brugbarhed. Den ene af de tre strategier er en ny metode: WSS[2]-logbogsmetoden, som er foreslået og anvendt i denne afhandling.

I artikel D er arbejderes gennemsnitlige aritmetiske langtidseksponering for 3,3'-dichlorobenzidiner i farvestøv ('ink fly') i to heatset trykkerier over et år, estimeret ved brug af logbogsmetoden (Olsen, 1994). Resultaternes afhængighed af anvendt prøvetagningsstrategi er undersøgt.

I artikel E beskrives og diskuteres en metode og en procedure til at bringe arbejderes eksponeringer under kontrol på virksomhedsniveau, i en bestemt branche eller på landsplan. WSS-logbogsmetoden er forslået, som velegnet til screening.

I artikel F er en metode beskrevet og udviklet til overvågning af at eksponeringer, der er bragt under kontrol, forbliver under kontrol, ved brug af passende statistiske tests.

Et mere uddybende referat af artiklerne, som indgår i denne afhandling, samt en sammenfatning er givet i den efterfølgende summerende rapport.

[2] WSS – Workers Self Sampling, identisk med SAE (Self Assessment of Exposure)

Contents

1. INTRODUCTION....3

2. SAMPLING STRATEGIES....5

2.1. Systematic sampling: 'Worst case'....5
2.2. Unbiased sampling:
2.2.1. Strategy 1: 'Measured 8h TWA strategy'....5
2.2.2. The logbook method....6
2.2.2.1. Strategy 2: Logbook + Process Concentration for calculating 8h TWAs....6
2.2.2.2. Strategy 3: Logbook + 8h TWA for calculating Process Concentrations....7

2.3. Exposure to vapours (exemplified by styrene)....8
2.4. Exposure to aerosols (exemplified by ink fly)....9

3. OVERVIEW OF PAPERS....10

3.1. Method development (vapours, exemplified by styrene)....10
3.2. Method development (aerosols)....12

3.3. Quantifying exposure to styrene....13
3.4. Quantifying exposure to aerosols....18

3.5. Bringing exposure under control....19
3.6. Keeping exposure under control....21

4. EXPOSURES AT THE WORKPLACE....22
4.1. Vapours....23
4.2. Aerosols....25

5. DISCUSSION....27

6. CONCLUSION....30

7. GLOSSARY AND ABBREVIATIONS....32

8. BIBLIOGRAPHY....36

9. PAPERS....39

PAPERS included:

[A] 'Uncertainty budget for measuring airborne styrene. A general method for estimating concentration of vapours in workers breathing zones during performance of a single process',
Nyeland ME, Holst E, Kristiansen J, Olsen E and Thyregod P
To be submitted

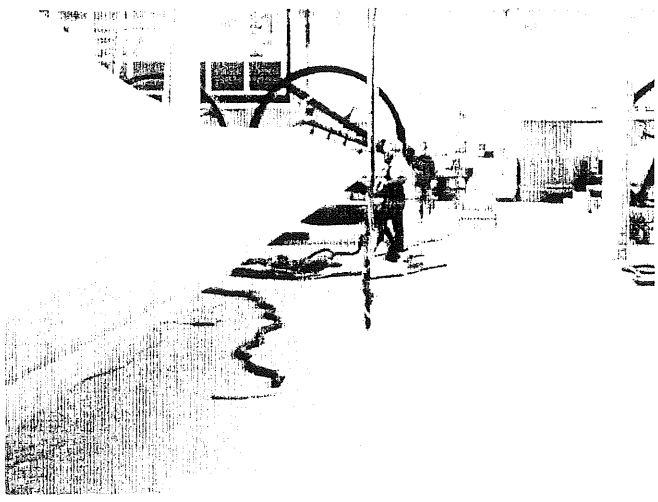
[B] 'A review on monitoring exposure to solid aerosols',
Nyeland ME, Olsen E and Christensen JM.
Submitted for publication

[C] 'Quantifying exposure to airborne styrene and the associated uncertainty depending on the sampling strategy applied',
Nyeland ME, Holst E, Olsen E and Thyregod P
To be submitted

[D] 'Exposure to ink-fly in two Danish heatset printing shops',
Nyeland ME, Hansen ÅM, Olsen E and Wallin H
To be submitted

[E] 'Exposure assessment and intervention – Bringing exposure under control',
Nyeland ME, Holst E, Olsen E and Thyregod P
To be submitted

[F] 'Monitoring a population of employees from the occupational environment',
Holst E, Nyeland ME, Olsen E and Thyregod P
Submitted for publication



From a windmill wing factory, during the process polishing (Hall III).

1. INTRODUCTION

Occupational exposures vary greatly over time, as well within- as between workers (Heederik *et al.*, 1991; Kromhout *et al.*, 1987; Peretz *et al.*, 1997; Rappaport, 1991; Tornero-Velez *et al.*, 1997). It has been observed that individual's daily exposures during a longer period e.g. a year is log normal distributed (Esmen *et al.*, 1977; Oldham *et al.*, 1952; Rappaport, 1991; Rappaport *et al.*, 1993; Ulfvarson, 1987). The long-term arithmetic mean air exposure concentration is the measure, which can be related to risk of adverse health effects due to chronic exposure for a single worker (Rappaport, 1991). To get a complete, quantitative measure of exposure for all workers, the most direct method would be to measure individual exposures of all workers all days during the exposure period considered (e.g. a year). However this is not possible due to practical and economic reasons. Various sampling strategies and statistical modelling of exposure are therefore applied. The goal is to get the most reliable estimate of workers mean exposure to one or more pollutants during a time period – minimizing the number of samples under the economic constrains. In general, it is supposed that the uncertainty due to the sampling strategy applied contributes with the major part of the total uncertainty when estimating workers long-term exposures.

The duty of health and safety authorities' is to ensure that the working environment is satisfactory. This is commonly done by controlling that no workers are exposed to a particular substance above the Occupational Exposure Limit (OEL) in force. OEL refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be exposed repeatedly to the given substance 8 hours day after day without experiencing any adverse effects American Conference of Governmental Industrial Hygienists (ACGIH, 2002). OEL is based on available information from industry, from human and animal experimental studies or from a combination thereof. Risk for adverse effects due to chronic exposure at the workplace is assessed by comparing data on long-term exposures with the OEL. To ensure that the welfare of the workers nation-wide is not endangered it is desirable to perform an exposure assessment followed by interventions, if needed, in a given line of industry, a given company or a given department as the first step to bring the exposure under control. This could be done by intervening at the group level e.g. by substitution of a hazardous substance with a less harmful one or by enhance ventilation in a working room. It can also be done at the individual level for instance by changing specific processes or changing their surroundings (e.g. local exhaust ventilation).

Different kinds of strategies depending on the purpose of the investigation can be applied in quantitative exposure assessment. One kind of approach is to estimate exposure at the individual level in which exposure of each individual is estimated. Another approach is to estimate the average level of a HEG's exposure, to be applied to all members of the group. In this case only a representative sample of the group are being sampled.

The purpose of the exposure assessment determines the choice of strategy. One purpose could be to estimate the average exposure of the group over time. This is appropriate for epidemiological studies. Another purpose could be to estimate the average exposure of individuals and compare this value to average exposures of e.g. other persons. This is suitable for studies in occupational hygiene, for improvements of the working environment or determining compliance with OEL.

In this PhD thesis, four kinds of measurement strategies are considered. A systematic sampling strategy 'Worst case strategy', and three unbiased strategies, based on random sampling:

- Strategy 1: 'Measured 8h TWA strategy' (Rappaport *et al.*, 1993; Rappaport *et al.*, 1995; Rappaport *et al.*, 1999)
- Strategy 2: 'The logbook method (**PC**)' (Olsen, 1994)
- Strategy 3: 'The logbook method (8h-TWA)' (Nyeland *et al.*, 2002a; Nyeland *et al.*, 2002b)

2. SAMPLING STRATEGIES

2.1. Systematic strategy: Worst case strategy

The sampling strategy suggested by European standard EN 689 called the worst case strategy is a practical method for sampling (European Commitee for Standardization (CEN), 1995). It has no theoretical base: the occupational hygienist is selecting workers to be measured which he or she suppose to be highest exposed. It is assumed that the 'worst case' situation appear the day measurements are done and that the 'worst case' can be identified preliminarily by the occupational hygienist, interviewing workers and managers, which is doubtful according to previous studies demonstrating that it was not possible for workers, managers and occupational hygienists to judge exposure levels without any quantitative data (Hawkins *et al.*, 1989; Kromhout *et al.*, 1987; Post *et al.*, 1991). Compared to random sampling, it has been shown that worst case data were biased with a factor of more than five (Olsen *et al.*, 1991). The rationale in worst case strategy is that if the highest exposure occur on measurement day and if this event can be predicted and identified by the occupational hygienist then it is possible to decide whether workers in general are too highly exposed or not. The worst case strategy can be used for determining that the exposure concentration is below the OEL, but cannot be used for demonstration of non-compliance with OEL. A high result may be caused by the worst case situation or because the long-term average is above the OEL, or both (Olsen *et al.*, 2002). Because it is biased to an unknown degree, data cannot e.g. be used to establish OEL or for epidemiological studies.

2.2. Unbiased strategy

2.2.1. 'Measured 8h-TWA strategy' (Strategy 1)

A way to stratify a random selection of people is on the base of homogeneous exposure groups (HEG) (Rappaport, 1991) or similar exposure groups (SEG) (Mulhausen *et al.*, 1998). The population investigated is divided into groups supposed to be exposed to approximately the same concentration level. Criteria for this division could for instance be that the workers have the same job titles, are exposed to the same agents or that they are working in similar surroundings with the same kind of ventilation. Often it is seen that HEGs are inhomogeneous (Rappaport *et al.*, 1993).

A method using random sampling for collecting data was proposed by Rappaport (Rappaport, 1991) in the present thesis called Strategy 1 as a reaction to the commonly used worst case strategy. Data are analyzed using the random effects model (Rappaport *et al.*, 1993; Rappaport *et al.*, 1995) or with explanatory variables such as process- and task related covariates using mixed models

(Nylander-French *et al.*, 1999; Rappaport *et al.*, 1999). Measurements can be performed as 8-hour measurements, handled by the workers themselves SAE*, (Self-Assessment of Exposure), distributed and collected by mail (Liljelind *et al.*, 2000; Rappaport *et al.*, 1999). Recently it has been shown that unbiased exposure data were collected by workers themselves by using this sampling measurement method (Liljelind *et al.*, 2001). Applying Strategy 1 it is possible to estimate the average within- and between-worker variations, when at least two measurements on each worker are carried out. Covariates, such as ventilation (local exhaust ventilation (LEV)/natural ventilation), work patterns (continuing/intermittent), working indoor or outdoor, etc. contributing to exposure, can be identified and investigated at a general level. Applying Strategy 1, exposure is estimated at group level.

2.2.2. The logbook method

2.2.2.1. Strategy 2: Logbooks + Process Concentrations for calculating 8h TWA

An alternative strategy is the logbook method, where exposure concentration and exposure time are measured separately. Data are collected from randomly selected workers. The Process Concentration (**PC**) for each process is estimated, by measuring different operators while they perform the process. Exposure time is measured by workers keeping logs on when they start and stop the different processes during the log period. A matrix for daily exposure concentration for each worker can be established, based on **PC** for each process performed during log period and the process exposure time (Δt_p). Stratifying on the base of processes often results in a reduction of the variability in data, which has been shown by Olsen (1994). A higher degree of accuracy is obtained on measurement result (a workers long-term arithmetic daily mean exposure), because a larger number of estimates for daily exposures can be obtained applying Strategy 2. The logbook method is based on process domain and time measurements (logbook) on the contrary to Strategy 1 and worst case strategy, in which exposure is measured in time domain (Olsen, 1994). Exposure estimates at the individual as well as at the population level can be obtained. 8h-TWA is calculated as: $8\text{h-TWA}=\sum \mathrm{PC}_p \, \Delta t_p$.

* SAE is not a suitable name for this kind of sampling. Workers are not doing any *assessment* - more correctly they are doing *sampling*.

2.2.2.2. Strategy 3: Logbooks + 8h TWAs for calculating Process Concentrations

A measurement method, based on the Logbook method, using 8h TWA measurements and logbooks to calculate Process Concentrations is proposed and applied in this PhD thesis. 8h TWA measurements using passive samplers can be used when applying this method. The need for an occupational hygienist present during sampling is thus reduced compared to Strategy 2. In Paper C it is shown, that applying this version of the logbook method, it is possible to calculate process concentrations from 8h TWA measurements.

When **PC**s of all processes have been calculated based on 8h TWA measurements and logbooks, individual long-term exposures for workers can be estimated on an even larger scale, based on logbooks and calculated **PC**s.

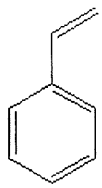
There is an economic benefit in applying Strategy 2 or Strategy 3, when **PC**s have been measured or calculated from 8h TWA. At this stage no further measurements are needed to obtain more exposure estimates, only time registrations in logbooks are needed. When implementing an exposure model obtained in one company to another company, it will, however, be necessary to validate the model, based on new measurements.

Data under Strategy 2 and Strategy 3 provide data to be used for identifying the highest exposed persons and data, which can identify the processes, which contribute the most to workers exposures at large. The methods are useful for monitoring a group of persons and to study changes in people's exposure and process concentrations over time. Information obtained can be used for decisions on interventions at the individual level to reduce exposure.

In the present PhD thesis, exposure to airborne substances at the workplace have been studied exemplified by vapours (styrene) in a windmill wing plant in the fibre glass polyester industry and aerosols (ink-fly) in two heatset printing shops.

2.3. Exposure to vapours (exemplified by styrene)

Styrene is classified by IARC as *possibly carcinogen to humans* (i.e. class *2B*) (IARC, 1994). Apart from the carcinogenic effect, such as provoking leukaemia and cancer in the pancreas, styrene has effects on the neurological system as have volatile organic compounds in general. Common symptoms are depression, concentration problems, fatigue and nausea. Styrene vapours may also lead to irritation of eyes, nose and throat. It is indicated that styrene has an effect on reproduction as well (Gezondheidsraad, 2001). It has been shown that exposure to styrene even in low concentrations (50-100 mg/m3) can cause adverse effects on health (Vaino *et al.*, 1977).



M:	104.16 g mol^{-1}
MP:	-30.6 °C
BP:	145.2 °C
Density:	0.906 g cm^{-3}
Vapour pressure:	
20°C:	0.6 kPa
25°C:	0.87 kPa
50°C:	3.2 kPa
80°C:	12.2 kPa

Figure 1 Styrene (C_8H_8). Physical properties of styrene monomer ((Weast, 1970)).
M – Molar Mass; BP – Boiling point; MP – Melting point.

Occupational exposure levels, measured both by air measurements and biological monitoring, have been highest in the manufacture of fibreglass-reinforced polyester products and lower in the production of styrene, polystyrene and styrene-based plastics and rubbers. In most parts of the industry, in general, the level of occupational exposure to airborne styrene has been found to be modest (<10 mg m^{-3}) (IARC, 1994).

The limit value for styrene in Denmark is 25 ppm (cm^3 m^{-3}) or 106 mg m^{-3} (Anon. 2000). It is a ceiling limit, which should never be exceeded.

2.4. Exposure to aerosols (exemplified by ink fly)

In the printing and painting industry, yellow pigments based on 3,3'-dichlorobenzidine (DCB) are used in large amounts. Pigment Yellow 12 (PY12) and Pigment Yellow 13 (PY13) are some of the most commonly used yellow pigments. Due to the very high speed in heatset printing, small droplets of ink (ink fly) are formed and made airborne and can, therefore, be inhaled by workers. The chemical structures and physical chemical properties of PY12 and PY13 are very similar. In theory, these pigments may be cleaved by azoreductases in the intestines or in human tissues and metabolised to DCB, which is suspected to be a human carcinogen. Exposure to PY12 and PY13 might be used as a model for exposure to other similar aerosols in the heatset printing industry e.g. red and blue pigment or carbon-black.

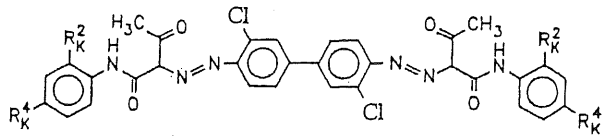


Figure 2. Molecular structures of the 3,3'-dichlorobenzidines (DCB), PY12 a PY13. For PY12, R_K^2 = H and R_K^4 = H, for PY13 R_K^2 = CH_3 and R_K^4 = CH_3 (Herbst *et al.*, 1997)

3. OVERVIEW OF INCLUDED PAPERS

3.1. Method development (vapours, exemplified by styrene)

[A] 'Uncertainty budget for measuring airborne styrene. A general method for estimating concentration of vapours in workers breathing zones during performance of a single process', Nyeland ME, Holst E, Kristiansen J, Olsen E and Thyregod P

In Paper A, an improved method has been developed to determine concentrations of vapours (styrene) in the breathing zone (process concentrations) and their uncertainties (**PC** ± *U*), where *U* is the expanded uncertainty, coverage factor $k = 2$, according to (BIPM, 1993). **PC** is estimated as a mean value of n PC_i measurements obtained using personal active sampling (SKC-pumps) to collect styrene on adsorbents (silica gel or Tenax). The styrene was desorbed using liquid desorption and analysed by gas chromatography using FID detector (GC-FID). In Paper A all uncertainty components are quantified and compared using an uncertainty budget and rules for combining uncertainties ($u = \sqrt{\sum c_i^2 u_i^2}$) according to GUM (BIPM, 1993).

Previously, a method for active sampling (SKC-pumps) of exposure to organic vapours was developed in which charcoal tubes was used as adsorbent and *N,N*-dimethylformamide (DMF) as desorption liquid followed by analysis using GC-FID (Johansen *et al.*, 1981). The method, however, has shown to be encumbered with large extrapolation errors and low recovery, when measuring exposure to styrene, especially for liquid concentrations below 200 µg/ml. In Paper A the method has been improved by increasing desorption efficiency, using a combination of DMF as desorption liquid and Tenax or silica gel as adsorbent.

Sampling, was done using personal active sampling (SKC-pumps, 222-85) equipped with Tenax (15/30mg, SKC cat. no. 226-35) or silica gel (75/150mg, SKC cat. no. 226-10), sampling time was 10-15 minutes. Sampling was done in duplicates in the breathing zone at different persons performing a single process. For illustration, **PC** of the process 'Stripping, in form' during the production of a windmill wing was estimated as well as its uncertainty. All uncertainty components were quantified and compared using an uncertainty budget.

Conclusions (Paper A):

Uncertainty in estimating **PC** = $\sum \frac{PC_i}{n}$ *was found to be 14% (relative standard deviation (RSD)).*

Uncertainty in estimating $PC_i = \frac{C_{i1} + C_{i2}}{2}$ *including: sampling on a person, transport, storage, pre analytical handling and laboratory analysis was found to be about 2% (RSD). The major contribution to* u_{PC_i} *the uncertainty of* PC_i *(a single measurement on an operator performing a single process) was liquid desorption.*

Figure 3 shows that uncertainty due to within- and between worker variability and variability in process emission is the major source of uncertainty, when estimating PC. *It is of note that it is the sum of variances of the different components that is shown in Figure 3. The uncertainties are not additive but the variances are.*

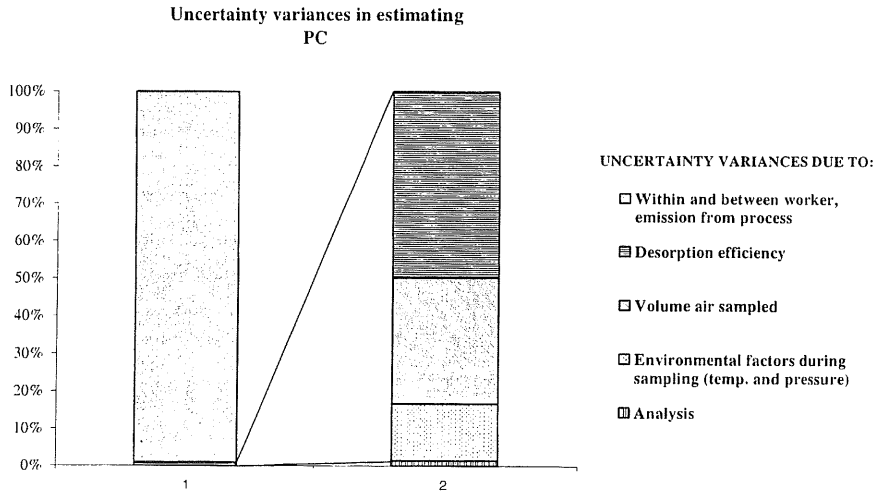


Figure 3. Contributions from uncertainty components (expressed as uncertainty variances) to the total uncertainty (variance) when estimating **PC**.
Column 2 is a close-up of the lowest part of column 1.

3.2. Method development (aerosols)

[B] 'A review on monitoring exposure to solid aerosols',
Nyeland ME, Olsen E and Christensen JM.

Paper B reviews the literature on particle behaviour in air and in the human airways, the sampling theory for aerosols, and sampling equipment, which is currently in use and commercial available.

The concepts and equations are given, which are necessary for understanding the often counter-intuitive behaviour of aerosols in the occupational setting and elsewhere. The mathematical manipulations of the equations have been kept at a minimum instead transport properties are illustrated by a series of calculations for aerosols consisting of water, minerals, and uranium.
The same concepts and equations are needed to explain and quantify the deposition of particle in the human airways and to design measurement devices. These devices are used for measuring the different aerosol fractions, which will deposit in different parts of the human airways.
A brief description of the human airways is given, which is adequate for the understanding of particles' deposition. The available methods for collecting airborne particles are described and it is discussed to what extend each type of equipment is sampling the aerosol fraction of interest.

Conclusions (Paper B):

Decisions on suitable sampling methods for aerosol sampling can be taken based on methods described in the review.

3.3. Quantifying exposure to styrene

[C] 'Quantifying exposure to airborne styrene and the associated uncertainty depending on the sampling strategy applied',
Nyeland ME, Holst E, Olsen E and Thyregod P

In Paper C, the long-term average daily exposure (8h TWA) to styrene for a single worker, working in a windmill wing plant, is estimated and the associated uncertainty quantified, depending on the sampling strategy applied. Subsequently major exposure sources are identified to be used for intervention. Three sampling strategies are applied: 'The measured 8h TWA strategy' (Rappaport *et al.*, 1993; Rappaport *et al.*, 1995; Rappaport *et al.*, 1999), 'The Logbook method (**PC**)' (Olsen, 1994) and 'The Logbook method (8h TWA)' (Nyeland *et al.*, 2002a; Nyeland *et al.*, 2002b)

Data obtained using the three sampling strategies are compared.

The strategies lead to the following measurements:

1. Strategy 1 ('Measured 8h TWA strategy') → 8h TWAs
2. Strategy 2 (The logbook method (logbooks + **PC**s measured)) → 8h TWAs
3. Strategy 3 (The logbook method (logbooks + 8h TWAs measured)) → **PC**s
   Subsequently applied on a larger scale (logbooks + **PC**(measured or calculated)) → 8hTWAs

For 8h TWA measurements, a method for passive or diffusive sampling of styrene in air was used (Health and Safety Executive, 1985). Samples were desorbed using thermal desorption followed by GC-FID analysis. Active sampling (using SKC-pumps) was used to measure the **PC**, using the method developed in Paper A. The active sampling method, using liquid desorption, has traditionally been the commonly used method for occupational hygiene measurements. An experiment in the field was designed in which passive sampling measurements (thermal desorption) was compared with active sampling measurements (liquid desorption) to calibrate the methods for validation of the new measurement strategy. The methods did correlate well within the estimated measurement uncertainty of active sampling method (Paper A).

Strategy 1 applied: 8h TWA, repeated measurements (2-4 pro person) of 39 randomly selected workers in three different departments (Hall I, Hall II and Hall III). Sampling method was passive

sampling (Health and Safety Executive, 1985). PROC MIXED, (SAS statistical software) was used to analyse data (Littell *et al.*, 1996), using departments as explanatory variable. Exposure levels in each of the halls were estimated. The estimates for each room are values for mean exposures of the population of workers. As each of the three halls are categorised as Homogeneous Exposure Groups (HEGs) according to Rappaports criteria (Rappaport, 1991), estimated GMs values of each hall are the best estimates for individual workers arithmetic mean exposure applying Strategy 1.

Strategy 2 applied: To validate the logbook method, 8h-TWA was obtained using Strategy 2 in parallel with the 8h TWA measurements of the 39 workers described above. Exposure measures did correlate well in Hall I (Figure 4).

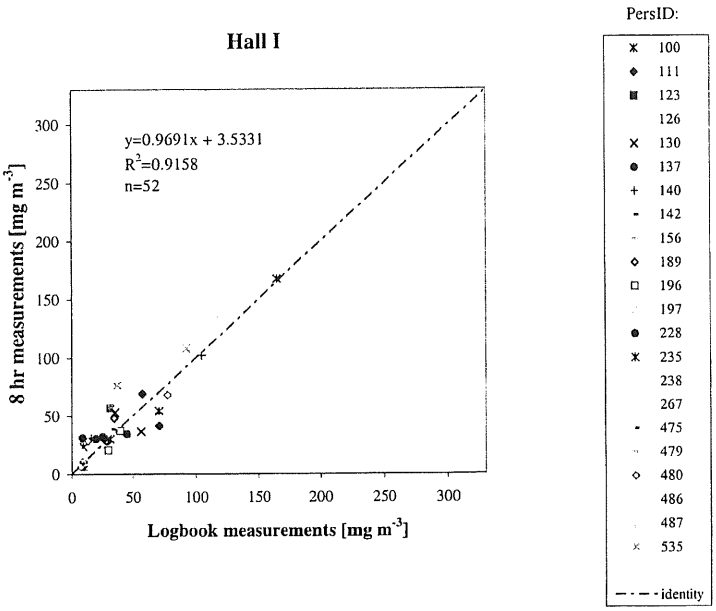


Figure 4. Correlation of 8h TWA estimated under Strategy 2 and 8h TWA concentrations measured. Single day measurements.

Measurements obtained in Hall II did not correlate well. It was not possible to motivate workers to fill in the logbooks in a proper manner. Time recordings obtained were thus too sloppy for any proper use.

In Hall III there was some correlation found, although not as good as in Hall I. Data obtained applying Strategy 2, seemed to be a little biased towards higher values. According to the logbook,

the majority of workers in Hall III did record time for each process including time spent on preparations.

Strategy 3 applied: Applying the logbook method (logbooks + 8h TWA concentrations measured) in Hall I, it was possible to solve the matrix for daily exposure concentration of each worker as a general linear model, using PROC GLM, SAS to estimate values of **PC**s. Figure 5 shows that uncertainties of **PC** estimated were found to be of the same magnitude, as the values obtained for **PC** measured. The number of measurements needed was reduced and much easier achieved compared to the traditional logbook method (Strategy 2).

PCs in Hall III were obtained as well. These estimates were associated with a much larger uncertainty (Paper C).

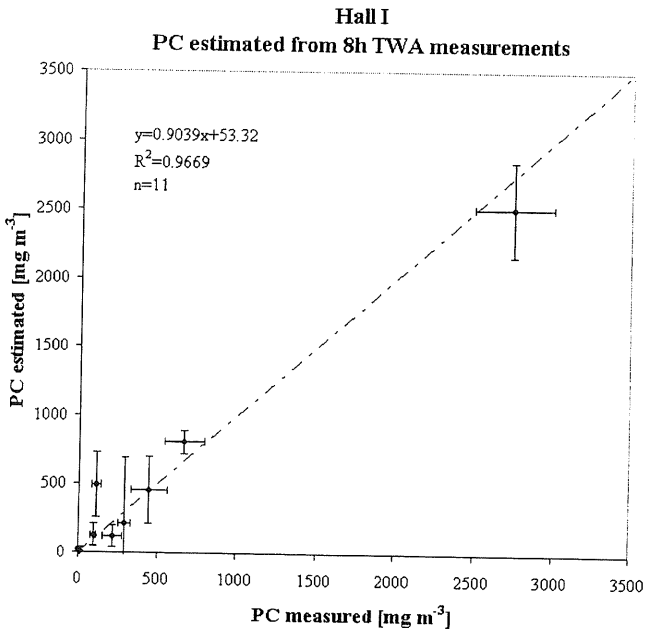


Figure 5. Correlation of estimated **PC**s (from 8h TWA measured + logbooks) and measured **PC**s of workers in Hall I. SDs are shown.

The validation of the logbook methods (Figure 4) shows that it is possible to estimate 8h TWA applying Strategy 2 or Strategy 3.

Logbooks had been distributed to all of the workers in the three departments during the log period, which was 3 separate weeks during a reference period of 6 months. Individual 8h TWAs during the log period were obtained applying Strategy 2 on data obtained for persons in Hall I. Strategy 3 was applied to obtain 8h TWAs for persons in Hall III. 840 estimated 8h TWA exposures were obtained for 328 workers (2-8 repeated measurements of each worker). This large amount of data was collected during a period of effectively 12 working days. Long-term arithmetic mean concentrations of individuals are estimated and subsequently major exposure sources are identified for intervention at the individual level.

Comparing the strategies applied

Uncertainty due to measurement procedure when estimating a single workers 8h TWA concentration **a single day**, is found to be larger applying the logbook methods (about 34%) compared to uncertainty in measuring an 8hTWA concentration (about 8%), as expected. Applying Strategy 1 the only uncertainty on the 8h TWA measurement of a single day is the uncertainty due to sampling, transport, storage and analysis. It is of note, that the measurement uncertainty (RSD = 8%) using passive sampling, and thermal desorption and the measurement uncertainty, using active sampling and liquid desorption (RSD found to be about 2% in Paper A), relates to different amounts of air sampled. RSD of the two measurement methods cannot be compared directly. Due to error propagation measurement uncertainty is expected to be much larger using active sampling (liquid desorption) for 8 hours (480 min/15 min = a number of 32 tubes would be needed) compared to passive sampling (thermal desorption).

When subsequently estimating the **arithmetic mean** exposure of the groups in Hall I, II and III applying the strategies, data for a larger number of days are obtained applying the logbook methods leading to a more accurate estimate of the individual arithmetic mean exposure compared to the estimate obtained applying Strategy 1. The logbook methods provide 8h TWA estimates of each worker for a large number of days of a very low cost, because only logbooks are needed, when **PC**s have been estimated.

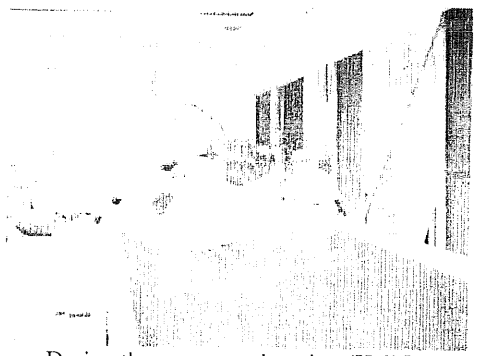
It is concluded that even though the uncertainty in estimating 8h TWA of **a single day** is found to be smaller under Strategy 1 (higher precision), the benefits are much larger applying Strategy 2 or 3, when estimating the long-term **arithmetic** 8h TWA **mean** exposure of an individual worker. Exposure data for a large number of days are obtained resulting in higher accuracy on measurement result. It is desirable to estimate individual exposures connected with the lowest possible

uncertainty, as it is the long-term arithmetic mean air exposure concentration, which is the measure that can be related to risk of adverse health effects due to chronic exposure for a single worker (Rappaport, 1991).

All three strategies provide answers to the question: are workers in general too high exposed?
In addition, Strategy 2 and Strategy 3 answer the question: which processes contribute the most to workers dose? Information for decisions on e.g. where to intervene most effectively is provided, applying Strategy 2 or Strategy 3. In case the purpose of the exposure assessment is to bring exposure under control, Strategy 2 and Strategy 3 are useful because they identify and quantify sources of exposure. Highly emitting processes or time spent at specific processes can be changed to reduce exposure and bring individual exposures under control.

Conclusions (Paper C):

- *All strategies applied provide information on exposure at group level*
- *Applying Strategy 2 and Strategy 3, more accurate estimates of the long-term mean exposure value at the individual level are obtained compared to Strategy 1.*
- *In addition, Strategy 2 and Strategy 3 provide quantitative information useful for decisions on interventions, information useful e.g. for bringing exposure under control.*
- *Strategy 3 can be applied obtaining estimated* **PC** *associated with uncertainties in the same order as* **PC** *measured. Sampling can be done by workers themselves (SAE). There is an economic benefit in applying Strategy 3, compared to the traditional logbook method (Strategy 2) because the consumption of occupational hygienist time at the workplace can be reduced. Strategy 3 is adequate for use as a screening method.*



During the process gelcoating (Hall I).

3.4. Quantifying exposure to aerosols

[D] 'Exposure to ink-fly in two Danish heatset printing shops',
Nyeland ME, Hansen ÅM, Olsen E and Wallin H

In Paper D, workers' exposure to 3,3'-dichlorobenzidines (in ink fly) during a year is estimated using the logbook method (Strategy 2). Results dependency on sampling strategy applied is studied.

Aerosols (ink-fly) were collected using a stationary high volume sampler (Gravicon VC25). Filters were extracted and analysed using HPLC, detected by UV-VIS. Individual exposures were estimated using the logbook method (time measurements) combined with the stationary measurements. Strategy A, was estimation of exposure using the logbook time measurements only for days where the concentration had been measured. Strategy B was estimating exposure using the logbook time measurements and mean values of stationary measurements obtained (logbook for days where the concentration was not measured). Strategy C was a combination of Strategy A and strategy B.
The variation in work patterns is the main source for variation in exposure.

Conclusions (Paper D):

It was proper to use Strategy C to estimate individual exposures using the logbook method. A specific group of workers (Helpers) were spending significantly more time in the room containing the printing machine. In case the intension was to reduce exposure of this group of workers, intervention could be done by changing the work patterns.

3.5. Bringing exposure under control

[E] 'Exposure assessment and intervention – Bringing exposure under control',
Nyeland ME, Holst E, Olsen E and Thyregod P

In Paper E, a procedure for bringing workers exposures under control on company level, in a specific line of industry or nationwide is described and discussed.

Figure 6 shows the procedure proposed.

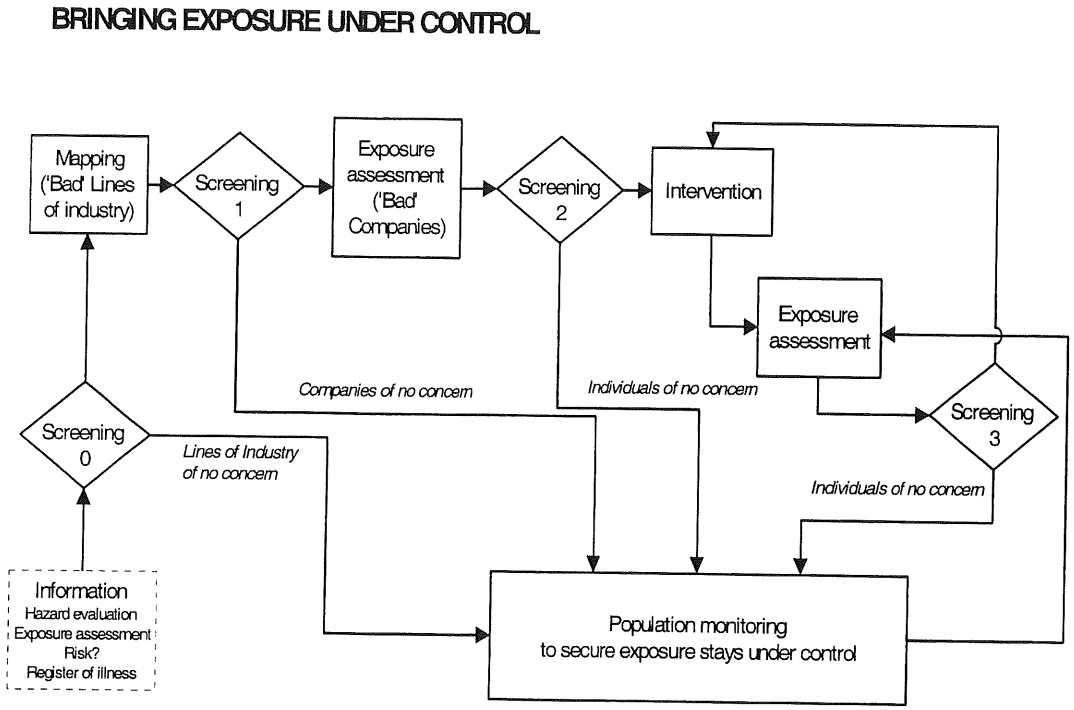


Figure 6. Flow diagram for bringing exposure under control

For exposure assessment at the individual level, measurement strategies such as Strategy 2 or Strategy 3 are adequate. These methods provide quantitative data for improvements in the workplace and interventions at process level, based on information on process concentrations and the time spent at each process. Depending on the size of the population investigated, it is decided which strategy to choose. Strategy 2 is suitable for both smaller and larger populations, but an occupational hygienist must be present during sampling, when measuring **PC**, and partly during the log period. Strategy 3 is suitable for larger populations in which time spent at the processes are such that the columns in the logbook-matrix are linearly independent. Passive sampling can be used, which can be done by workers themselves (SAE), for which a new word is introduced: WSS (Workers Self Sampling). In this case Strategy 3 is called: The WSS-Logbook method.

The need for measurements is reduced prospectively, when **PC**s have been estimated. The individual exposure of a large number of people can be estimated, from logbooks and the previously estimated **PC**s. There will be no need for further measurements unless something happens leading to changes in processes, ventilation etc.

Conclusions (Paper E):

Strategy 1 gives no data to be used for intervention at the individual level. It is concluded that both Strategy 2 or Strategy 3 are suitable for exposure assessment in case the purpose is to bring exposure under control at the individual level, depending on the size of the population and the 'design' of the study. Work pattern (time spent at different processes) should preferably be such that the columns in the logbook-matrix are linearly independent to obtain reliable estimates for **PC**, *applying Strategy 3. Strategy 3 is appropriate for use as a screening method.*

3.6. Keeping exposure under control

[F] 'Monitoring a population of employees from the occupational environment',
Holst E, Nyeland ME, Olsen E and Thyregod P

In Paper F, a system is described for monitoring that exposures which have been brought under control, stays under control, using adequate statistical tests.

Methods to monitor a population of workers exposed to a hazardous agent are outlined. Each worker is characterized by a statistical distribution of TWA values and the distribution characterizing the population is a compound distribution of individual distributions. Relevant parameters chosen are the probability, p, that a randomly selected worker has a TWA concentration exceeding the limiting value (LV), together with the mean of the TWA values in the population. Under the assumption that the compound distribution is log normal, statistical tests are developed for the probability that a randomly selected worker has a TWA value exceeding the LV. Relations between the criteria for these parameters have been calculated. Statistical tests have been developed for testing whether the relevant parameters in the compound distribution are exceeding limits of concern. Confidence intervals for the relevant parameters are provided.

Conclusions (Paper F):

A system for monitoring that exposure brought under control, stays under control, using adequate statistical tests has been developed.

4. EXPOSURES AT THE WORKPLACE

In this part of the thesis a short description is given on the object of measurement: exposures at the workplace.

There is a large variability in the exposure level from day to day at workplaces within and between different lines of industry, different companies, departments and persons. It is important to be aware of the variability connected to the measurements in the working environment. The variability can be illustrated by a hierarchical catalogue of exposure distributions. When measuring exposure in the working environment, it is important to note that the object of measurement is not a single value, but a distribution of values. Figure 7 shows different sources of variation to consider when estimating exposure for a hazard which could be a given substance at the workplace e.g. vapours or an aerosol. The six 'upper' boxes describes a 'natural' variation or variation of the object itself. The last box describes uncertainty due to measuring exposures.

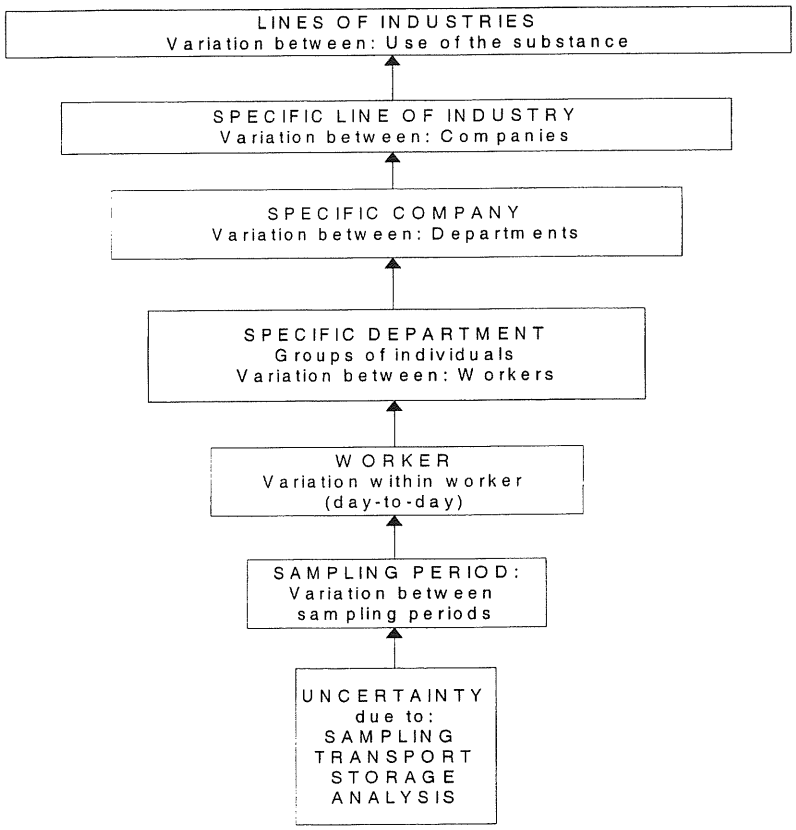
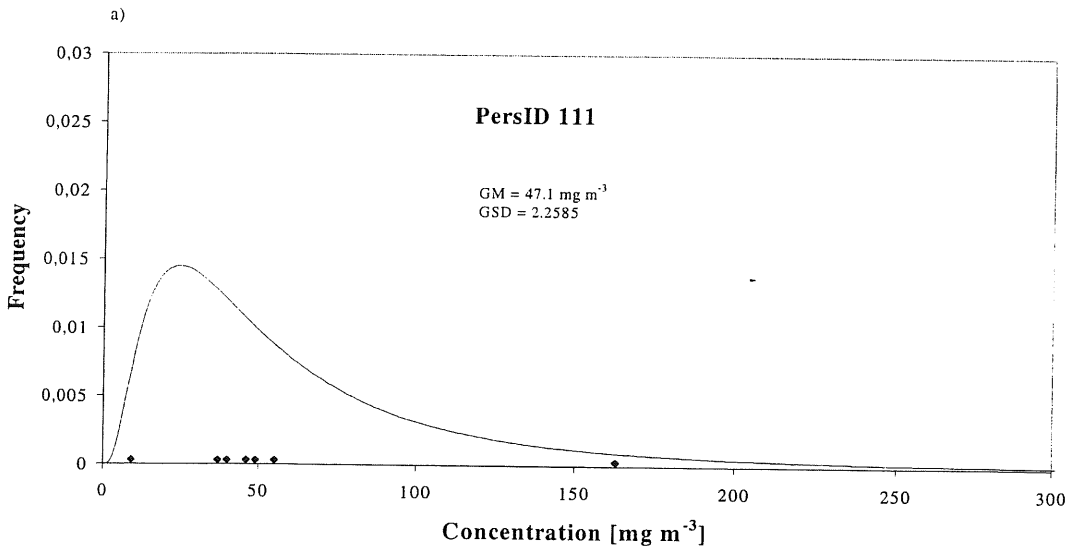


Figure 7. Exposures in the working environment - a hierarchical catalogue of distributions. (Nyeland et al. 2002, 'Exposure assessment – Bringing exposure under control').

Even in an ideal situation in which perfect measurements of all persons were obtained, the differences illustrated in Figure 7 will exist. It is important to note that the object of measurement is not a single value, but a distribution of values. For instance when assessing a persons exposure for a given substance, the question raised is not: 'What is today's exposure?', but rather: 'What is the mean exposure over a period?' or 'Between which values do we find 95% of the daily exposures?'. For a group of workers in a given industry, exposed for a given agent, it has been observed that there is a factor of 20-30 between the lowest and highest measurement (Kromhout *et al.*, 1993).
To illustrate how exposures variate at the workplace, some examples are given below on exposures to vapours (styrene) and aerosols (ink-fly). Individual workers' estimated exposures obtained during the log period, are shown. Exposures were found to be approximately lognormal distributed and thus individual exposures are fitted to a log normal distribution curve. Daily TWA values obtained during the log period for each individual are shown as black diamonds (◆).

4.1. Vapours

Specific workers individual daily exposures to styrene in the fibreglass-reinforced polyester industry, production of windmill wings have been measured applying Strategy 2 (Figure 8a, b, c and d).



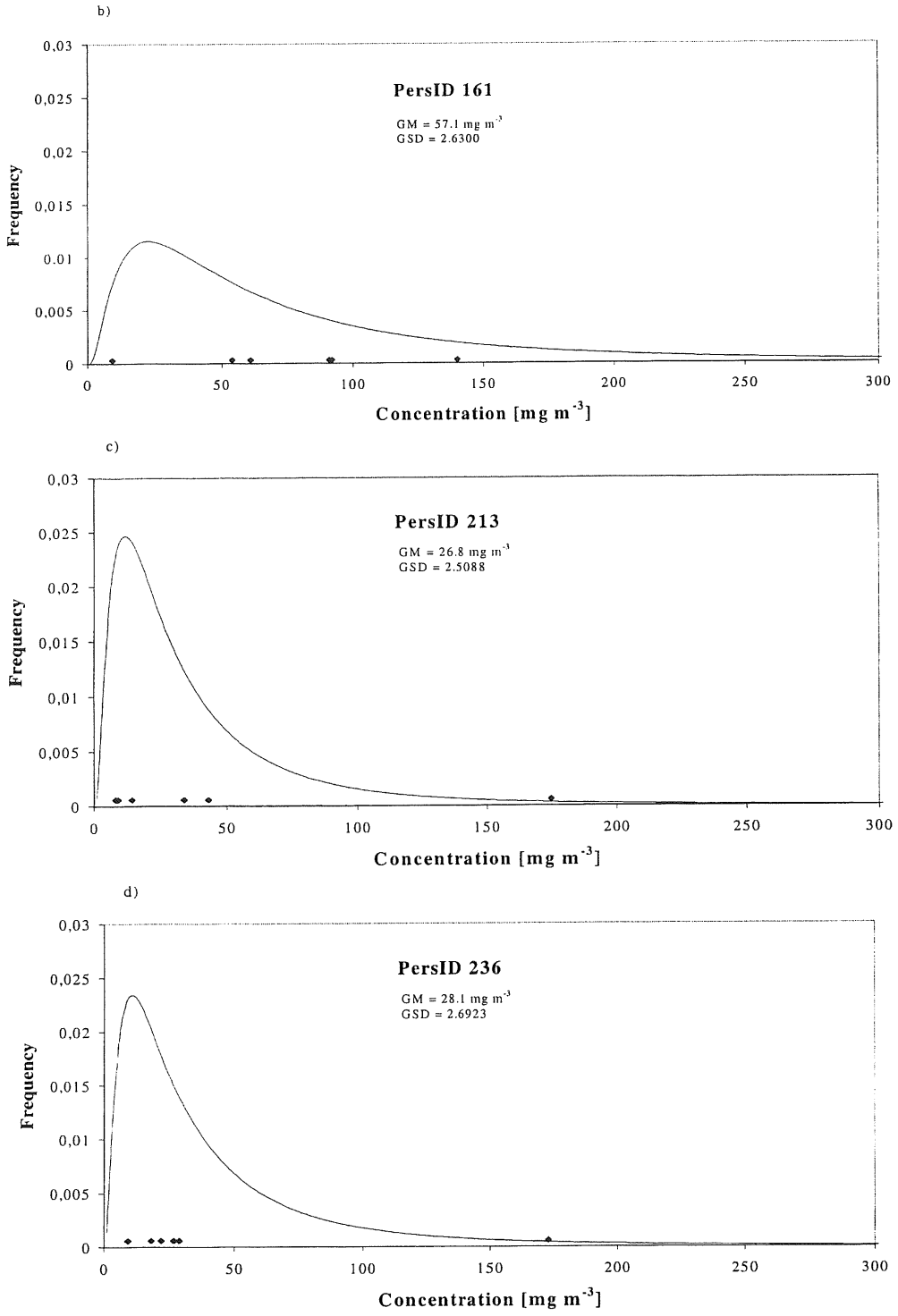
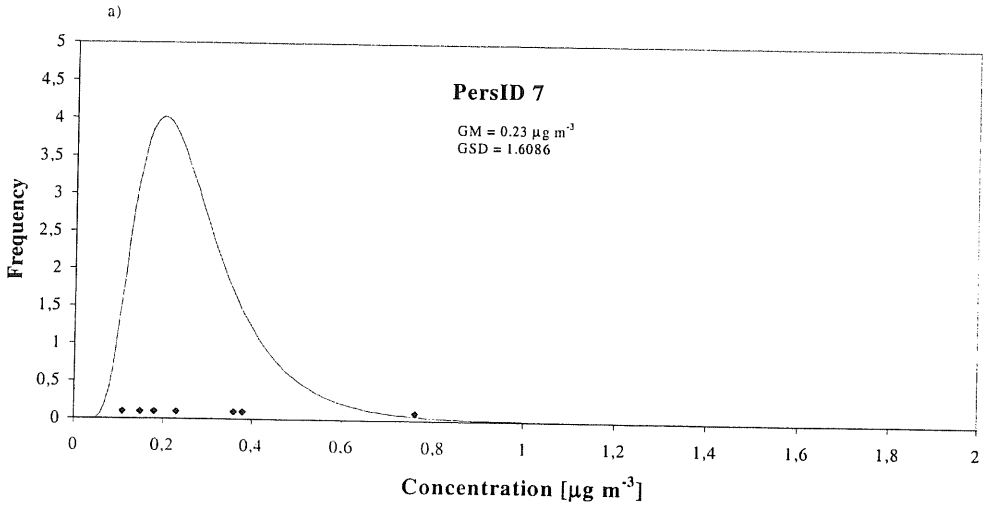


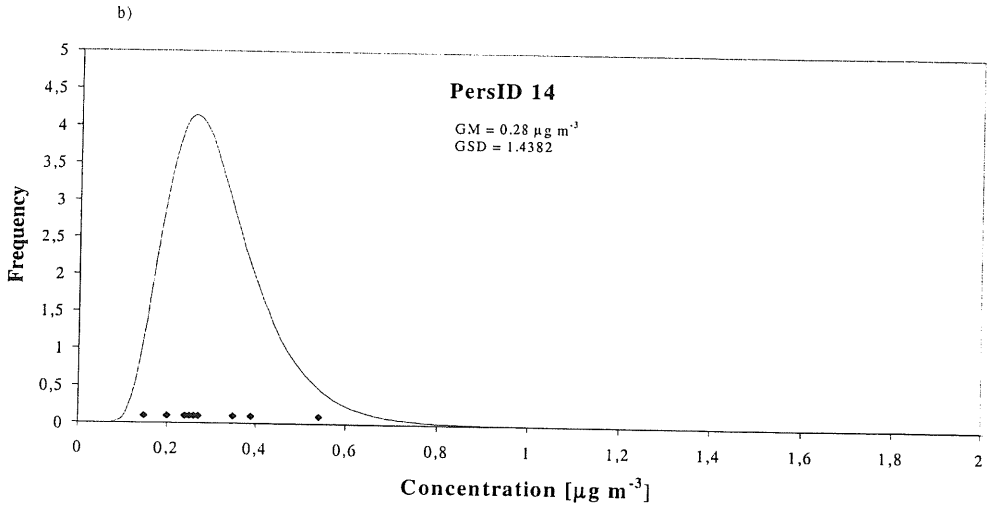
Figure 8a, b, c and d. Individual 8h TWA exposure distributions of exposure to styrene, y-axis is frequency in fraction/[mg m^{-3}].

4.2. Aerosols

Specific workers individual daily exposures to 3,3'-dichlorobenzidines ink-fly in a heatset printing shop have been measured applying Strategy 2.

In Figure 9a, b, c and d, the distribution of the exposures for ink-fly of pigment yellow of four workers during the log period are shown.





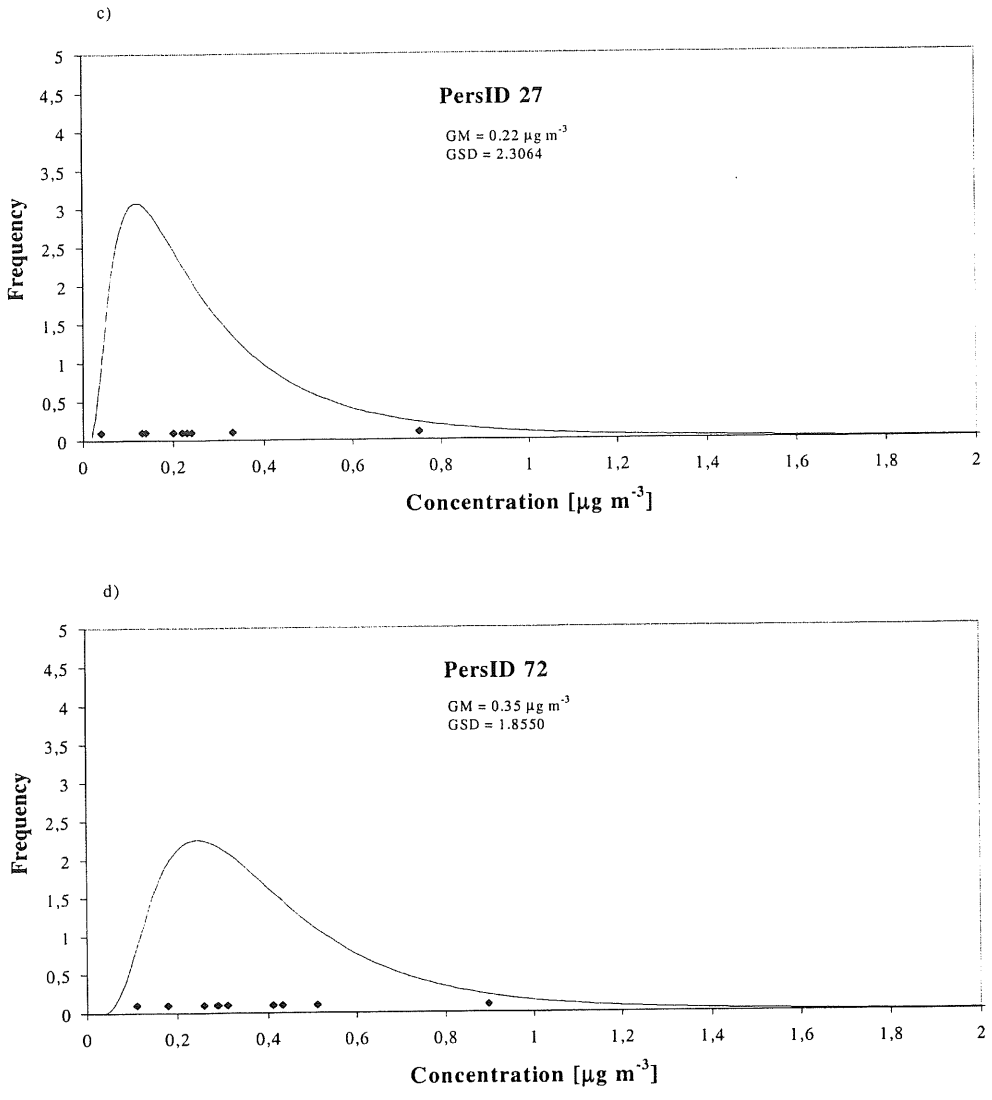


Figure 9a, b, c, d. Distributions of exposures to ink-fly (yellow pigment),
y-axis is frequency in fraction/[µg m^{-3}].
Individual 8h TWA exposures of workers in two heatset printing shops, during the log period.
a, b and c are from Printing shop 1, d is from Printing shop 2.

5. DISCUSSION

Methods for estimating exposure to vapours and aerosols in the working environment have been developed, proposed and applied in the present PhD study. A method for bringing exposure under control is proposed together with a program for monitoring that exposure, which has been brought under control, stays under control.

The purpose of an exposure assessment determines the choice of strategy applied. Estimating the long-term arithmetic mean air exposure concentration is the goal and a central task for exposure assessments, because it is the measure, which can be related to risk of adverse health effects due to chronic exposure for the single worker. This goal is fulfilled by all of the three unbiased strategies applied in this thesis, but the techniques to obtain the goal differs as do the associated uncertainties.

During the last decade Strategy 1 (Rappaport, 1991; Rappaport *et al.*, 1993; Rappaport *et al.*, 1995) has become the most commonly applied measurement strategy to obtain unbiased data for exposure assessments. Applying this strategy a large number of data are needed to develop meaningful and informative empirical models (Kromhout, 2002). In 1994 another approach, the logbook method (Strategy 2), to obtain unbiased data for exposure assessment was proposed (Olsen, 1994). An extended version of the logbook method, Strategy 3, is proposed and applied in the present thesis (Paper E and Paper C). Traditionally new methods are validated against well known, well tested methods. In the present thesis the new measurement strategy (Strategy 3) is thus validated, tested and compared to the measurement strategies Strategy 1 and Strategy 2. In Paper C a study is done in which all three strategies are applied to obtain a unique dataset to be used for comparison.

Applying Strategy 1, only two measurements pr. worker are needed for estimating average σ_W^2 or σ_B^2 (the average within- and between-worker variance) in the exposure model. In contrast, the logbook methods provide larger number of exposure measurements pr. worker e.g. 15 days. A better estimate of the arithmetic mean exposure of the individual worker is obtained under Strategy 2 although the uncertainty in estimating exposure of a single day is larger compared to Strategy1. This is in agreement with the observations in Paper C, in which uncertainty on the logbook estimates (estimates of general exposures in the three departments) is reduced compared to the uncertainty on the estimates obtained, applying Strategy 1. Applying Strategy 1 the object of measurement is the exposure of a population of workers and the measurand is the population

distribution of individual arithmetic mean exposures. This sampling strategy is adequate when it is possible to divide workers in homogeneous exposure groups (HEGs) e.g. fulfilling the criteria defined by Rappaport (Rappaport 1991). In Paper C, all of the three departments fulfil this criteria, which is very coarse – since it is observed that workers are actually very inhomogeneous exposed in the three departments. Exposure information obtained applying Strategy 1 can only be used for intervention at the general level.

Strategy 3 is suitable for exposure assessment at workplaces in which the work pattern preferably are such that the columns in the logbook matrix are linearly independent, to obtain reliable estimates for **PC**s. In general, the benefits of the logbook method are highest when workers work patterns varies substantially from day to day, when workers with different job titles perform the same processes or perform the same process in different fractions of the working day.

In general, when applying the logbook method (Strategy 2 or Strategy 3), it is important to be aware of how the work is organised at the workplace. The design of the logbook is important to obtain reliable estimates for exposure. All processes must be properly defined. Workers shall be carefully informed on the purpose of the log keeping and most important that it is confidential. In case workers receive substantial exposure from neighbour processes, logbooks have to be more detailed designed, including information on neighbouring processes. Preliminary measurements can be carried out to check for exposure from neighbour processes.

In Paper C the logbook methods could not be applied in Hall II because the workers in Hall II were low motivated and the resulting logbook registration was sloppy. In Hall III time registration by the logs were kept more coarse compared to logbook registrations in Hall I. Time registrations for each process were in general too long compared to the actual time spent performing the process, leading to slightly overestimated 8h TWAs.

As the 'worst case strategy' is a systematic strategy, biased towards higher values, it is not recommended for use, when performing an exposure assessment to estimate workers exposure e.g. for establishing OELs or for epidemiological use.

Data obtained applying Strategy 1 are suitable to be compared to OEL at group level (HEG) to decide whether workers are high, medium or low exposed.

The logbook methods provide data, which can be used for comparing compliance with OEL at individual level as well as at group level. Data obtained applying the logbook method can be used for risk management for controlling workers exposure. An important advantage applying the

logbook method is that quantitative data are obtained which can be used for intervention at individual level.

When the purpose of performing an exposure assessment is to obtain data for estimating workers exposure to be used for a monitoring program, the strategies discussed in the present thesis (except from the 'worst case strategy'!) supports one another very well. When measuring on a population, both Strategy 1 and the logbook strategies answer the question of whether workers are too high exposed. This information can be used for decisions on general improvements such as general ventilation, general improvements on personal protective equipment for the HEG or substitution. Applying the logbook methods it is possible to identify and quantify emission from processes performed and therefore provide quantitative data for improvements. Such data are useful for interventions to bring exposure under control at the individual level as described in Paper E, e.g. the working pattern for the individual worker or emission from a process can be changed to reduce exposure.

Under Strategy 1, measurements can be handled by workers themselves (SAE) and only two samples per worker are needed. Strategy 2, in which **PC**s are measured by an occupational hygienist, sampling of measurements thus seems to be more expensive compared to Strategy 1.
In Paper A it is shown that measurement uncertainty is much less than the within- and between worker variance when performing occupational hygiene measurements. In Paper A, a method for measuring concentration of airborne styrene using active sampling has been improved. Uncertainty in the measurement method has been reduced compared to the previously method applied (Johansen et al. 1981). But yet desorption is the major source of uncertainty in the measurement procedure. The uncertainties of active sampling and liquid desorption are much larger than uncertainties of passive sampling and thermal desorption.
In the present thesis, a method for estimating workers exposure (Strategy 3) is proposed (Paper E) and applied (Paper C). Sampling is done using passive samplers for 8h TWA measurements plus logbooks. Sampling can be done by workers themselves as Workers Self Sampling ('the WSS-Logbook method'). **PC**s are calculated from logbooks and 8h TWA measurement results as a general linear model. In Paper C it is shown that it is possible to obtain estimates of **PC**s matching the value of measured **PC**s with uncertainties of the same magnitude. The economical costs using this version of the logbook method are reduced compared to the traditional logbook method,

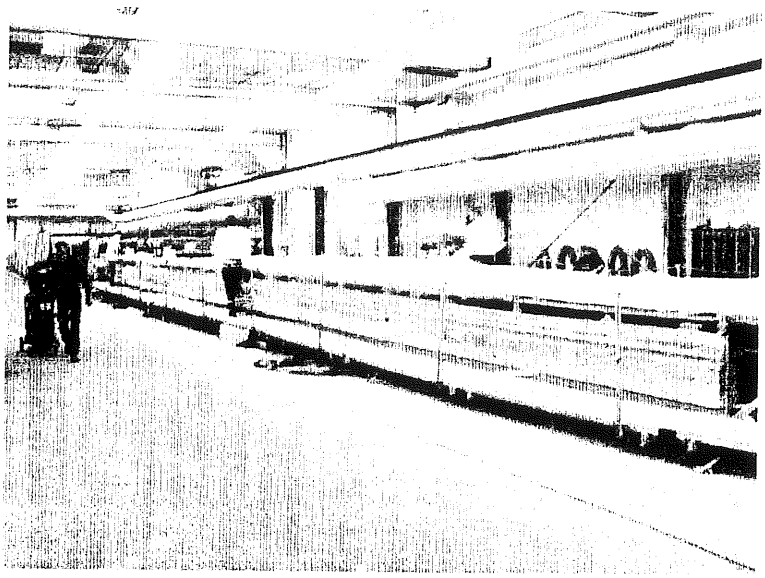
Strategy 2, because the need for an occupational hygienist presence during sampling is reduced, especially when using the WSS-Logbook method.

Once **PC**s are established the 8h-TWAs for a large number of workers can be estimated at low cost as only logbooks are needed. A way to improve the logbook method further is to introduce electronic logbook registrations, which presumably will increase motivation among the log keepers. The WSS-Logbook method can be applied for measuring exposure to other contaminants than the ones studied in the present thesis. The method is applicable when measuring exposure to all kinds of airborne agents - chemical or biological. The only requirement apart from the one mentioned above (sufficient variability in work pattern to solve the matrix), is that the sampling method has to be simple and easy to handle. Otherwise an occupational hygienist has to be present during sampling.

6. CONCLUSION

Methods for estimating exposure for vapours or aerosols in the working environment have been developed, proposed and applied. A sampling strategy, the WSS-Logbook method, for estimation of workers individual exposure has been developed, proposed and applied based on workers self sampling using passive sampling and log keeping. The strategy is appropriate for studies including a larger number of subjects. Applying the strategy, a large number of daily exposure estimates can be obtained at low cost. The data are useful for decisions making at the individual level in risk management e.g. for bringing exposure under control.

A method for bringing exposure under control before monitoring has been proposed together with a program for monitoring that exposure, brought under control, stays under control.



At the windmill wing factory, during the vacuum casting (Hall II).

7. GLOSSARY AND ABBRIVIATIONS

8h TWA	The 8-hour time-weighed average concentration. A measure which can be related to OEL
ACGIH	American Conference of Governmental Industrial Hygienists
aerosols	Various disperse systems in air, such as dust, fog, clouds, mist, fumes and smoke
AM	Arithmetic Mean. Is the correct parameter for evaluating cumulative exposure as dose is proportional to AM, independent on the distribution. As uptake $\propto$ exposure concentration (C), AM $\propto$ dose.
analytical methods	Methods used in laboratory analysis of samples. These are chemical analysis techniques used to identify and quantify an agent collected on sampling media
between-worker variability	The worker-to-worker variability in exposures
BP	Boiling Point
breathing zone	A zone of air in the vicinity of a worker from which air is breathed. Personal breathing zone measurements of air contaminant concentrations frequently are made by directly placing monitors in the breathing zone of workers (personal sampling).
compliance study	A study in which the purpose is to evaluate compliance with governmental standards. For occupational exposures compliance with the regulatory OEL
DCB	3,3'-Dichlorobenzidine
DMF	Dimethyl formamide
epidemiology	The study of epidemics. Branch of medical science concerned with the study of patterns of disease amongst large groups of people. It includes, in the present context, determination of the relationships between exposure of a group of employees to hazardous substances and the resultant effects on their health.
explanatory variables	Variables in a variance analysis, which explains some of the variability in data

exposure	A subjects contact with a chemical, physical (noise), or biological agent. Occupational exposures can occur via several pathways, including inhalation, ingestion and skin contact.
exposure assessment	The process of defining exposure profiles and judging the acceptability of workplace exposures to environmental agents.
GC-FID	Gas chromatograph equipped with a flame ionization detector
GM	Geometric Mean. The nth rooth of the product of n values. The GM is the median (50% quantile) of log normally distributed data.
GSD	Geometric Standard Deviation. The antilog of the standard deviation of the log transformed data (measure of variability for a lognormal distribution).
GUM	Guide to the Expression of Uncertainty in Measurement (ISO) (BIPM, 1993)
HEG	Homogeneous Exposure Group. A group of workers who experience agent exposure supposed to be similar. Categorizing workers into these groups often involves categorization by process, job description, and agents. Further separation can be attained dividing on the basis of task analysis.
HPLC	High-Performance Liquid Chromatography
IARC	International Agency for Research on Cancer. Lyon, France.
intervention	Interposition or interference to change one state to another. For occupational exposures, intervention could be done by substitution, changing ventilation or changing work pattern
LEV	Local Exhaust Ventilation
LOC	Limit of concern
LOD	Limit of detection
LOQ	Limit of quantification
logbook	A diary for each worker in which process during the working day are pre printed. Times for start and stop for performing each process are recorded by workers during the working day.
LV	Limiting Value

M	Molar mass
monitoring	Keeping under surveillance. In occupational hygiene this could be workers exposure to secure that a population of workers exposure e.g. stays under control.
MP	Melting Point
occupational exposures	A worker's contact with a chemical, physical, or biological agent. Occupational exposures can occur via several pathways, including inhalation, ingestion, skin contact and whole body radiation
OEL	Occupational Exposure Limit. Some substances may have several OELs e.g. an 8-hour time-weighted average concentration and a short-term exposure limit (STEL)
PC	Process Concentration. A mean value of emission from a single process, measured in the breathing zones of different workers while performing the single process. Measured on different days.
PC_i	Process Concentration of a single measurement i, when estimating **PC** (the AM of several PC_i's - the expected value of PC_i is **PC** $E(PC_i)$).
PY12	Pigment Yellow 12
PY13	Pigment Yellow 13
qualitative analytical analysis	Analytical chemical analysis of a substance in order to a certain the nature of its constituents
quantitative analytical analysis	Analytical chemical analysis of a substance in order to determine the amounts or proportions of its constituents
RSD	Relative Standard Deviation ($SD/\bar{x}$)
SAE	Self Assessment of Exposure in other words: Workers Self Sampling. Sampling is done by workers themselves.
sampling	Collection of samples
sampling strategy	A plan to guide actions for sampling to accomplish a stated goal
SD	Standard Deviation
SEG	Similar Exposure Groups.

SKC	A company that serves the Industrial Hygiene, Safety, Environmental and Occupational Health markets by providing air sampling instruments and sample collection media.
statistical modelling	Using statistics and data collected to produce a statistical model to describe a phenomenon
storage	Storage of sample in laboratory before analysis
strategy	A plan to guide actions to accomplish a stated goal
transport	Transport of sample from field to laboratory
TWA	Time-weighted-average (concentration)
u	Uncertainty of an uncertainty component
U	The overall uncertainty, including a coverage factor.
unbiased strategy	A strategy leading to measurements which are unbiased because workers to measure are randomly selected
uncertainty component	A source of uncertainty contributing to the overall uncertainty of the result.
UV-VIS	UV-VIS absorption spectroscopy
vapour	The gaseous state of a substance, which is liquid or solid at room temperature and atmospheric pressure.
within worker variability	The variability (e.g., day-to-day, minute-to-minute) of exposure to an environmental agent for an individual worker.
worst case strategy	A practical strategy for measuring exposure, without any theoretical base. Exposure measurements are carried out on workers expected to be the highest exposed.
WSS	Workers Self Sampling. Identical with SAE.

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Paper [A]

UNCERTAINTY BUDGET FOR MEASURING AIRBORNE STYRENE
A general method for estimating concentration in workers breathing zones during performance of a single process

[A] UNCERTAINTY BUDGET FOR MEASURING AIRBORNE STYRENE

A general method for estimating concentration of vapours in workers breathing zones during performance of a single process

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ABSTRACT

An improved method has been developed to determine concentrations of vapours (styrene) in the breathing zone (process concentrations) and their uncertainties (**PC** ± *U*), where *U* is the expanded uncertainty, coverage factor $k = 2$ (BIPM, 1993). **PC** is estimated as a mean value of n PC_i measurements obtained using personal active sampling (SKC-pumps) to collect styrene on adsorbents (silica gel or Tenax). The styrene was desorbed using liquid desorption and analysed by gas chromatography using FID detector (GC-FID). All uncertainty components are quantified and compared using an uncertainty budget and rules for combining uncertainties ($u = \sqrt{\sum c_i^2 u_i^2}$) according to GUM (BIPM, 1993).

Previously, a method for active sampling (SKC-pumps) of exposure to organic vapours was developed (Johansen *et al.*, 1981). The method, however, has shown to be encumbered with large extrapolation errors and low recovery, especially for low amounts sampled (<200 μg ml^{-1}). The method has been improved by increasing desorption efficiency, using a combination of DMF as desorption liquid and Tenax or silica gel as adsorbent.

Sampling was done using personal active sampling, sampling time was 10-15 minutes. Sampling was done in duplicates in the breathing zone at different persons performing a single process. For illustration, **PC** of the process 'Stripping, in form' during the production of a windmill wing was estimated as well as its uncertainty. Uncertainty in estimating $\mathbf{PC} = \sum \frac{PC_i}{n}$ was found to be 14% (relative standard deviation (RSD)). Uncertainty in estimating $PC_i = \frac{C_{i1} + C_{i2}}{2}$ including: sampling on a person, transport, storage, pre analytical handling and laboratory analysis was found to be about 2% (RSD). The major contribution to u_{PC_i}, the uncertainty on PC_i (a single measurement on an operator performing a single process), was liquid desorption.

Keywords: Uncertainty budget, styrene, exposure assessment, active sampling, liquid desorption

INTRODUCTION

Styrene is a hazard and it is classified by IARC as *possibly carcinogen to humans (2B)* (IARC, 1994). Apart from the carcinogenic effect styrene possess such as provoking leukaemia and cancer in the pancreas, styrene has effects on the neurological system as volatile organic compounds in general and the respiratory system. Styrene is used as a cross linking agent primary in the fibreglass reinforced polyester industry, in the glue and rubber industry. It is one of the most widely used monomers mainly in the production of polystyrene and co-polymeric products and resins such as acrylonitrile-butadiene-styrene resins, styrene-butadiene rubbers and latexes and unsaturated polystyrene resins (IARC, 1994). Styrene is also a component in cigarette smoke and automobile exhaust and in low levels it may occur naturally as well in foods (Johanson *et al.*, 2000).

Occupational exposure levels for exposure to styrene, measured both by air measurements and biological monitoring have been highest in the manufacture of fibre glass-reinforced polyester products (exposure to airborne styrene: 40-400 mg m^{-3} (IARC, 1994)) and lower in the production of styrene, polystyrene and styrene-based plastics and rubbers. In most parts of the industry, in general, the level of occupational exposure to airborne styrene has been found to be modest (<10 mg m^{-3}) (IARC, 1994).

Exposure to styrene can thus constitute a risk for adverse health effects and thus limit values are established for styrene. In Denmark the OEL is 25 ppm (106 mg m^{-3}), which is a ceiling limit that should never be exceeded (Anon. 2000). When comparing a result of a measurement to the OEL the guidelines in (International standard ISO/FDIS 10576-1, 2001) should be followed. According to these it is necessary to quantify and estimate the uncertainty on the measurement result.

When estimating individual 8 hour daily exposure (the Time Weighted Average Concentration) using the logbook method (Olsen, 1994), exposure time measurements (time spent at each process during the working day) and exposure concentrations at each process (**PC**) are obtained separately. Time measurements are obtained by registration of time intervals for each process in logbooks by workers during the day. The process concentration (**PC**) is defined as a mean value of the concentration in the breathing zone of workers performing a specific process during a specified period (the reference period) e.g. 6 months. **PC** is estimated as personal samples in the breathing zone on different workers, performing the same process on different days during the reference period. Workers are selected randomly, to obtain representative measurements.

The vision in this paper is to estimate the concentration of styrene in the air and the corresponding uncertainty of the estimate, when performing a specific process. The strategy to fulfil the vision is to obtain the most reliable estimate of the process concentration during the reference period, with the smallest uncertainty on the measurement result. When quantifying all uncertainty components contributing to the total uncertainty on the measurement result, it is possible to assess where to intervene in the measurement process to bring down the total uncertainty. Uncertainty components from the different steps going from strategy and sampling through transport, storage, pre analytical handling, analysis and calibration to the final measurement result, should thus be mapped and quantified.

A way to list, quantify and compare all possible uncertainty components is using an uncertainty budget. Usually uncertainty budgets are made only for the sampling procedure and analysis of the sample. It is possible to include uncertainty due to sampling strategy applied as a higher level in the uncertainty budget, in case sampling has been performed in a suitable manner (Nyeland *et al.*, 2002).

Uncertainty on measurement result, when estimating exposure concentration for styrene when performing a specific process (the process concentration) during production of windmill wings in the fibreglass reinforced polyester industry, is investigated and quantified in the present study.

Personal exposure to airborne organic vapours at the working place is usually sampled and measured using either passive or active monitors, adsorbing the compounds on a suitable solid adsorbent followed by desorption of the compounds from the adsorbent before analysis on gas chromatograph (GC) (Delcourt *et al.*, 2001). In the present study, a method for sampling and measuring styrene using active personal sampling is described, and improved. Previously at the National Institute of Occupational Health in Denmark a method has been developed using charcoal tubes, using *N,N*-dimethylformamide (DMF) as desorption liquid before analysis (Johansen *et al.*, 1981). The method, however, has shown to be very imprecise when applied to exposure to styrene, due to that extrapolation propagate the errors, especially for lower concentrations (< 200 $\mu g\ ml^{-1}$). An experiment, to study the effect on recovery depending on choice of adsorbent and desorption liquid, is described in Appendix A ('The Desorption Efficiency Experiment'). An improved method for measuring concentration of styrene in air to lower uncertainty on the measurement result introduced by desorption, is suggested.

OBJECTIVES

The first objective is to develop an improved method to determine process concentrations of styrene and to quantify their uncertainties (**PC** ± U). A second objective is to quantify all uncertainty components, using an uncertainty budget ($u = \sqrt{\sum c_i^2 u_i^2}$) in accordance with the provisions in the Guide to the Expression of Uncertainty in Measurement (GUM)(BIPM, 1993).

METHODS AND RESULTS

Procedure for styrene sampling

A flow sheet of the procedure for measuring and estimating the process concentration is illustrated in Figure 1. Sampling plan, sampling, transport, storage, desorption and analysis are included.

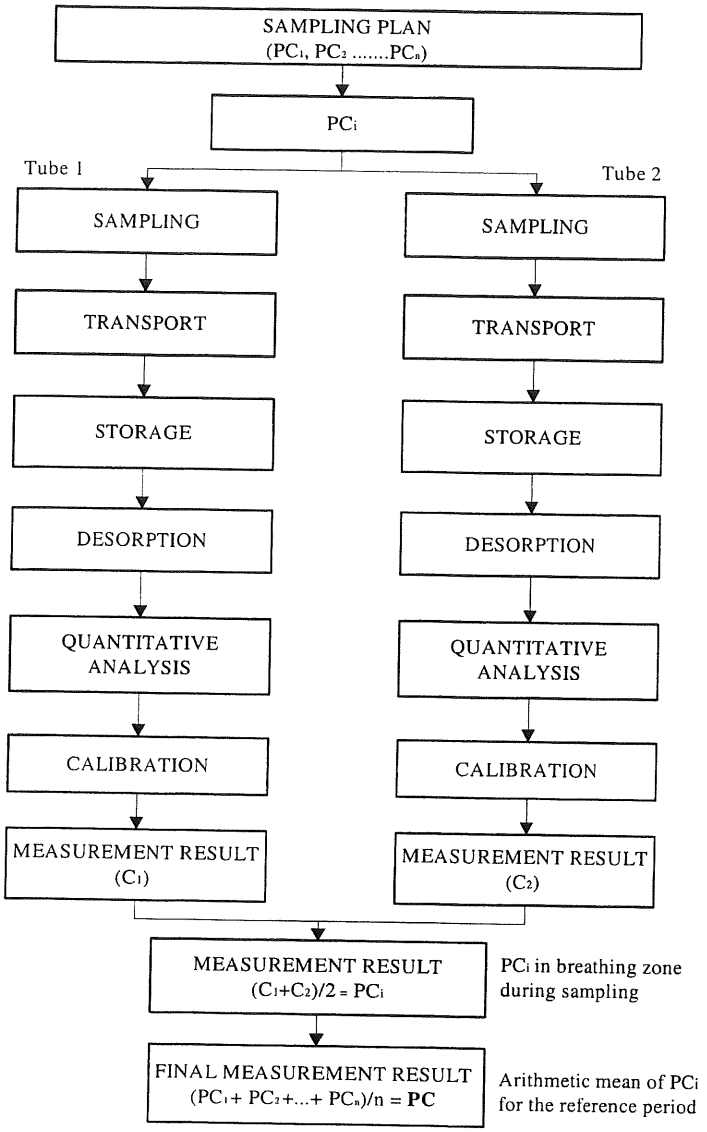


Figure 1. Flow diagram of the procedure when estimating and measuring a process concentration of styrene in air for a specific process. C_1 and C_2 are measurement results on tube 1 and tube 2; PC_i is the measurement result of one sampling; **PC** is the final measurement result (the arithmetic mean of PC_i of n samplings).

Sampling plan: Windmill wing plant, the process 'Stripping, in form', in which workers were standing in the windmill wing form, stripping off plastic folio after vacuum casting was ended. Samples were collected at different times of the year during a period of 6 months (the reference period), on randomly selected workers performing the specific process.

Sampling: Personal, active sampling using SKC-pumps (222-85, 20-50 ml min^{-1}), calibrated before and after each measurement day. Silica gel tubes (75/150mg, SKC cat. no. 226-10) or Tenax tubes (15/30mg, SKC cat. no. 226-35) were used for adsorbent tubes.

Transport: A tube was broken and stored by the samples for each measurement day as a blind test. Samples were stored in a transportable refrigerator (4°C).
Storage: Stored in refrigerator (4°C) for 1-4 weeks before desorption and analysis.

Desorption: Desorption liquid was DMF (*N,N*-dimethylformamide) purchased from Rathburn Chemicals, Scotland, UK. Procedure for desorption was done according to method described by (Johansen *et al.*, 1981). Samples were desorbed in 1 ml DMF, at 25°C for 24 hours before analysed.

Analysis: Samples were analysed on a gas chromatograph, autosystem XL (Perkin Elmer), equipped with a flame ionisation detector (FID) and a capillar column (Chrompack, WCOT Fused Silica (CP-Sil 8 CB), CP7452, length 25 m). Temperature: 70 - 110°C; 110 - 180°C. Injection volume: 1,0 uL. Styrene (>99%) was purchased from Merck Eurolab.

Uncertainty budget for styrene sampling
The uncertainty of the method for determination of styrene in air, described above, in which liquid desorption is an important factor, has been evaluated according to the procedure described in the Guide to the Expression of Uncertainty in Measurement (GUM) (BIPM, 1993). An uncertainty budget is set up in which uncertainty sources contributing to the total uncertainty, are evaluated systematically, quantified and compared. Uncertainties of all links through the traceability chain have been quantified.
A spreadsheet method proposed by Kragten, using a numerical method of differentiation, has been used to simplify calculations of combined standard uncertainty from input standard uncertainties and a known measurement model ((Kragten, 1994), (EURACHEM, 2000)).

Each level shown in the flow diagram consists of several subgroups of uncertainty sources contributing to the total uncertainty on the measurement result. These are illustrated in the cause and effect (or Ishikawa) diagram in the Appendix B, Figure B1, and described in more details in the present section.

In Appendix H (Table H1 – Table H8), uncertainties of the components in each of the levels in Figure 1 are estimated. Each level is described and studied below.

Uncertainty components contributing to the total uncertainty on the measurement result are inserted in a spreadsheet (Kragten, 1994) in Appendix I, Table I1-I12, in which standard uncertainties and relative influence to the total uncertainty of each component are calculated of all 12 measurements (PC_i) in the sampling plan.

The model of the estimate of **PC**, $M_{estimate}$, can be described as a function, F, including the effects, f, involved:

$$M_{estimate} = F(M_{measurement}, f_{sampling}, f_{transport}, f_{storage}, f_{desorption}, f_{analysis}, f_{calibration}) \quad (1)$$

Where $M_{estimate}$ is the value of the estimate of **PC** and $M_{measurement}$ represents results of the individual measurements (PC_i).

Corrections for effects involved, described in more details, includes:

$f_{sampling}$: Variations in emission from process
Within and between worker variation
Homogeneity of the air in the breathing zone of worker
Pumps: Use in the field (reading)
Drift
Environment: Pressure and Temperature

$f_{transport}$: In refrigerator

$f_{storage}$: In refrigerator or freezer

$f_{desorption}$: Desorption of sample, pre analysis

$f_{analysis}$: Short term effects (repeatability)
Long term effects (repeatability)

$f_{calibration}$: Calibration Curve (instrument)
Determination of desorption efficiency (calibration)
Calibration of pumps (determining PF (Pump factor))

Producing standard
Molar mass

Estimation of uncertainty when estimating the process concentration (**PC**)

The measurand, when measuring the process concentration, **PC**, is defined as the mean value of concentration of the contaminant in the breathing zone of the worker during the reference period, done by repeated measurements on a worker (or different workers) performing the given process. Uncertainty due to variations in emission from the process and variations within and between workers are included in this uncertainty, as well as all other uncertainty components in the flow diagram, Figure 1. To quantify this part of the uncertainty, due to process and worker condition, first it is necessary to quantify all other uncertainties.

A model to describe the estimated **PC** (a mean value of n measurements) is suggested:

$$\mathbf{PC} = \delta_s + \sum_{i=1}^{n} \frac{[D_i + PC_i]}{n} \qquad (2)$$

Where δ_s is a possible systematic difference in average concentration in the tube position (workers right or left hand side) during sampling
D_i is the deviation from **PC** at the i'th measurement (different day, different workers etc.)
PC_i is the mean value of C_{i1} and C_{i2}, the concentrations according to tube 1 and tube 2 of duplicates during the i'th sample.

In the present study exposure to styrene during the process 'stripping' is considered. It is a process performed during production of windmill wings, in which the worker is stripping off folio in the windmill wing form after vacuum injection process is ended and the polyester is hardened. The process takes about 15 minutes, exposure level is high about 2½ times the Danish OEL for styrene. Workers are wearing personal protection equipment (protection suit and fresh air masks) when performing this process.

The process concentration has been estimated based on 12 personal measurements. All measurements were sampled on different workers working in the Foundry Hall in a specific windmill wing plant. Samples were collected on different days in a period of 6 months. Silica gel (SKC Cat. No. 226-10, Lot. No. 1838) was used as adsorbent for eight of the measurements, Tenax (SKC, Cat. No. 226-35, Lot. No. 1290) was used as adsorbent for three of the measurements.

The uncertainty of estimating the process concentration has been estimated below.

Estimation of uncertainty of estimating **PC** *(homogeneity of air in breathing zone (δ_s))*

All measurements were done in duplicates. A pair of tubes were placed in the breathing zone of a person and exposed simultaneously in positions 1 cm apart using two independently calibrated pumps. The position of each tube, right or left hand side of the worker, was recorded. No bias due to a concentration gradient in air was found when using a sign test on all measurements of all processes in the production of windmill wings. In Figure 2, the relative difference between tube pairs of all measurements obtained (from different processes) are shown. The values have been sorted in numeric, decreasing order. Differences observed can be due to inhomogeniety of the air in the breathing zone and uncertainty due to laboratory analysis. The variability in difference between tube pairs observed is about 3% (RSD) on each sampling, which is about the same as the calculated analytical uncertainty and may therefore be ascribed to be caused by analytical uncertainty. It was thus decided not to consider any contribution from inhomogeneity of air in breathing zone (Appendix H, table H1).

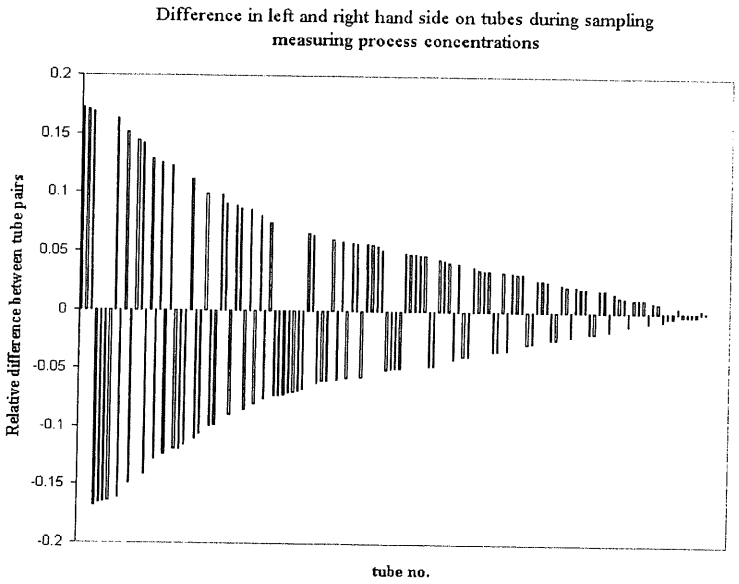


Figure 2. Relative difference in concentration sampled on tubes right and left hand side on worker, when measuring process concentrations

Estimation of uncertainty of estimating **PC** *(variation in emission from process and within- between worker ($\overline{D}$))*

Measurements obtained (PC_i) to estimate **PC** are shown in Figure 3.

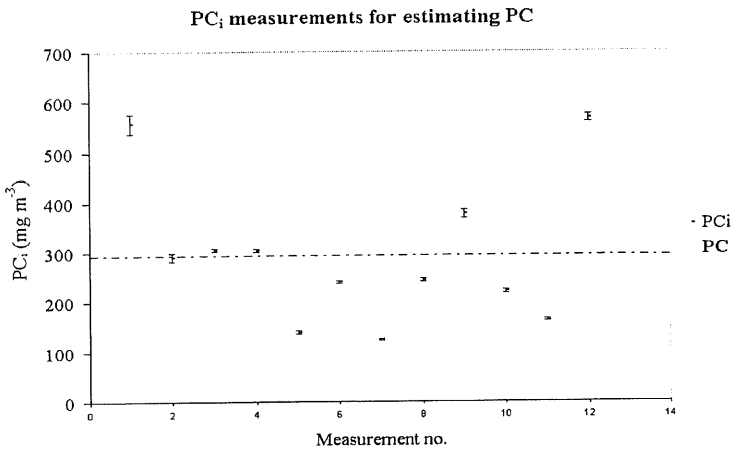


Figure 3. PC_i's used to estimate **PC**. Values of PC_i measurements and standard deviations are shown. The mean value (**PC**) is indicated.

As described above it is necessary to quantify all other uncertainties in the uncertainty budget to quantify the uncertainty due to variations in emission from the process and variations within and between workers, $\overline{D}$.

In Appendix I, p.13, **PC** and the associated total uncertainty are estimated. A mean value of the measurement uncertainty from each PC_i is estimated. Applying a scheme of analysis of variance (Table 1), these values have been used to estimate uncertainty of $\overline{D}$.

Table 1. Analysis of variance to estimate uncertainty of $\overline{D}$.

	Sum of Squares	Mean Square		
Between (D)	230713	$20974 \sim \sigma^2_{Di}$	$\bar{\sigma}_{Di} = 144.84$	$\sigma_{\overline{D}} = 41.81$
Within (Measurement uncertainty)	626	$52.1 \sim \sigma^2_{PCi}$	$\sigma^2_{\overline{PC}} = 4.35$	$\sigma_{\overline{PC}} = 2.08$
Total	231339			

Uncertainty in estimating **PC** is equal to: $u_{PC} = \sqrt{2.08^2 + 41.81^2} = 41.86$ mg m^{-3}. Uncertainty due to process and worker effects is thus $\sigma_{\overline{D}} = 41.81$ mg m^{-3}.

Estimation of uncertainty of estimating PC_i ***(a single measurement)***

The concentration of styrene sampled is determined as:

$$\text{Concentration [mg/m}^3\text{]} = \frac{\text{Amount of styrene sampled [mg]}}{\text{volume of air sampled [m}^3\text{]}} \quad (3)$$

The model function of determining the concentration of styrene in the air sampled in one tube is shown below (eq. 4). The air drawn through has been converted to a standard condition.

$$C = \frac{\left(\frac{\text{area}_{sample} - a}{b}\right)\frac{1}{DE}}{\left(\frac{(\text{Counter}_{stop} - \text{Counter}_{start}) \times PF}{1000}\right)\left(\frac{296}{T}\right)\left(\frac{P}{1013}\right)} \quad (4)$$

Where a is intersection with y-axis (calibration curve); b is the slope (calibration curve); PF is the pump calibration factor; DE is the desorption efficiency (recovery); T is the temperature (K); P is the pressure (hPa)

The result of one measurement on a process (PC_i) is a mean value of the duplicates (C_1, C_2). The model function is extended to:

$$PC_i = \left(\frac{\left(\frac{\text{area}_{C_1} - a}{b}\right)}{\left(\frac{(\text{Counter}_{stop,C1} - \text{Counter}_{start,C_1}) \times PF_{C_1}}{1000}\right)} + \frac{\left(\frac{\text{area}_{C_2} - a}{b}\right)}{\left(\frac{(\text{Counter}_{stop,C2} - \text{Counter}_{start,C2}) \times PF_{C_2}}{1000}\right)} \right) \frac{1}{2} \left(\frac{1}{DE_{C_{12}}}\right)\left(\frac{1}{\left(\frac{296}{t}\right)\left(\frac{P}{1013}\right)}\right) \quad (5)$$

reflecting that the environmental conditions (temperature and pressure) affected both tubes.

The process concentration during the reference period (e.g. 6 months) is estimated as a mean value of n measurements collected during that period: $\mathbf{PC} = \overline{PC_i} = \frac{(PC_1 + PC_2 + \ldots + PC_n)}{n}$, which is the actual measurement result (described above in the section 'Estimation of uncertainty when estimating the process concentration').

Estimation of uncertainty of sampling (volume of air sampled, environmental effects, break through)

Sampling of styrene vapours was done, by pumping a volume of air through a tube containing solid adsorbent, as described above. Calibration was done before and after each sampling day or week to be aware of any possible changes (drift). No bias due to drift was observed according to data obtained during the reference period. Calibration of pumps is described below ('Estimating uncertainty due to calibration').

Uncertainty due to use of pumps during sampling is estimated in Appendix H, Table H2.

Measurements have been corrected for environmental effects (temperature, pressure) according to equation 4 and 5. Pressure was obtained from the Danish Institute of Metrology (DMI), measured in Karup, Denmark. Temperature was measured during each measurement day using the same thermometer, calibrated using a standard thermometer.

Instrument uncertainty for temperature and pressure are estimated in Appendix H, Table H2.

In Table 2 the influences of environmental effects are considered, minimum and maximum values of temperature and pressure, obtained during the reference period, are used to calculate deviation from the corrected value according to equation 4:

Table 2. Environmental effects on the measurement result C, for a measurement of the process 'Stripping'. Influence of minimum and maximum values of the environmental effects during the reference period are considered.

		C [mg/m^3]	Deviation from corrected value (%)
Corrected	296 K 1013 hPa	290.2	-
Temperature (K)	293.5 (min) 1013 hPa	287.7	1.0
	296 (max) 1013 hPa	290.2	0
Pressure (hPa)	1003 (min) 296 K	287.3	1.0
	1033 (max) 296 K	295.9	1.0

Temperature and pressure seem to have minor effect on the measurement result, less than 1%. Compared to the relative standard deviation the environmental effect is very small. Due to the fact that all measurements in the present study were corrected according to equation 4, uncertainty due

to environmental effects is not otherwise included in the uncertainty budget, only instrumental uncertainty.

Influence on measurement result due to possible break through was investigated designing an experiment in which break through on Tenax tubes were studied (Appendix C, 'The Tenax tube Capacity Experiment'). To avoid loss due to break through, it was decided to exclude measurements in which content of styrene in control layer exceeded 15% of the total content on the adsorbent.

Estimation of uncertainty due to transport

At each sampling day, a tube was cracked for a blind test, carried and stored with the samples. Samples were stored in a transportable refrigerator in the end of a sampling day and during transport back to the laboratory, transferred to a refrigerator and stored until further handling and analysis. No waste due to transport should be expected according to the storage experiment. No contamination of any of the blind tests was observed.

Estimation of uncertainty due to storage

Possible influence on samples due to storage (in refrigerator or freezer) was investigated in 'The Storage Experiment', Appendix D. No significant changes due to storage in a period of 6 weeks were observed.

Estimation of uncertainty due to desorption

Desorption of styrene from the adsorbent was done by pouring the exposed sorbent into a vial adding 1 ml of desorption liquid. The vial was closed with a septum cap and stored at 25°C for 24 hr before analysis. The uncertainty due to desorption did not seem to be dependent on load, when using silica gel or Tenax as adsorbent and DMF as desorption liquid.

Uncertainty due to desorption of the sample is estimated from repeated measurements of tubes spiked with identical amounts of styrene, desorbed and analysed on GC (according to 'Calibration due to loss during desorption', below).

Analytical uncertainties

Uncertainties associated with the analysis using the gas chromatograph are those coming from the automatic sampling from the vial, injection in the port of the GC, uncertainty in the GC response, the integration of the area below the peak observed (e.g. due to overlap from other compounds in the sample) etc. All samples were analysed using double injections. Based on these injection duplicates, uncertainty in injection and instrument has been quantified in Appendix H, Table H5. No bias was found between the results obtained in the first and the second injection, according to a sign test performed.

Repeatability of the analysis method was estimated. Short term effects during a period of 2½ days and nights were studied making an experiment in which 60 vials (2 injections per vial), containing identical solution, was analysed immediately after one another. The short-term period was matching the period of a normal series of analysis of samples. Uncertainty of injections and uncertainty in the instrument are included (double injections). Results are shown in Appendix E, Figure E1. No cyclic variation is observed, but a tendency to a small, systematic variation is observed (approximately ± 1%).

Long-term effects were studied using an in house reference material (IHRM) (at two concentration levels – low and high, stored in a freezer) on all days of analysis. Results from a period of 6 months, were plotted in a Westgard plot, Appendix E, Figure E2, using the computer program WinAMIQAS for method evaluation (Anon. 1999). It seems as if there is a possibly slight drift during that period, less than 0.5% (RSD). Thus the standard uncertainty corresponding to a possible drift is less than 2%, which was considered to be negligible.
Standard uncertainty due to long-term effects of both high and low concentrations were found to be approximately 1.8%, however it was decided to use the standard uncertainty of the short-term effects in the uncertainty budget.

LOQ of the method has been determined to be 6.1 μg $tube^{-1}$ (5.85×10^{-2} μmole $tube^{-1}$), using WinAMIQAS (Anon. 1999).

Uncertainties due to repeatability are calculated in Appendix H, Table H5.

Estimation of uncertainty due to calibration

Calibration of GC. The calibration curve was determined using weighted regression ($1/\mu^2$), based on five concentration levels, two solutions produced for each level, each solution injected four times in the GC. Uncertainty in *a* (intersection with *y*), and *b* (the slope) has been estimated using WinAMIQAS (Anon. 1999). Estimates are shown in Appendix H, Table H6. Uncertainties in producing standard solutions, described below, are included in the uncertainty on the calibration curve.

Calibration due to loss during desorption. In Figure 4, a flow diagram illustrating the method for determining desorption efficiency to calibrate or correct the measurement result, due to recovery, is shown. The adsorbent, spiked with a certain concentration of styrene, was desorbed in 1 ml desorption liquid in a vial, closed and stored at 25°C for 24 hr before analysed. A vial containing 1 ml DMF 'spiked' with the same concentration of styrene, was made and analysed parallel (100% vial). Desorption efficiency or recovery was determined.

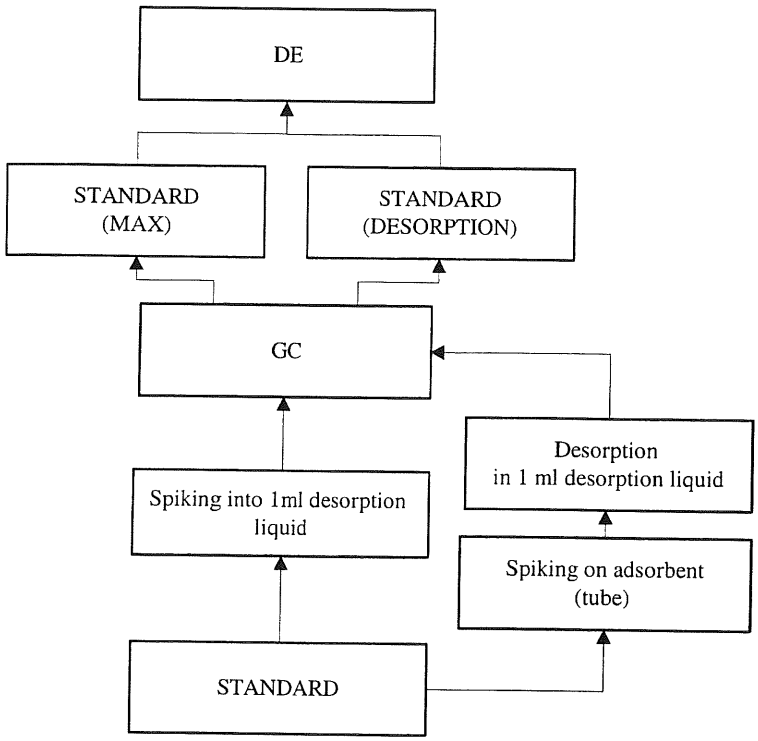


Figure 4. Flow diagram illustrating the method for determination of desorption efficiency.

Calibration of pumps. Pumps were calibrated by using a soap bubble flow meter as a primary standard. Calibration was done before and after each sampling day or week to be aware of any possible changes (drift).
Uncertainty due to determination of pump factor is estimated in Appendix H, Table H6.

Estimating uncertainty in producing standard solutions

Purity of reagents used for producing standard solution.

According to supplier, purity of the batch of styrene used was found to be 99.9%. Certificate of analysis from Merck of the current batch is included in the Appendix F, Figure F1. A GC-mass spectra of the pure styrene was recorded, verified that the styrene was the only content (Appendix G, Figure G1).
Standard solutions for each concentration level for the calibration curve was produced by 'weighting out' styrene directly in a glass flask (100 ml), and accordingly filling up with solvent. Subsequently dilutions were avoided to minimize uncertainty. Solutions were prepared separately to avoid correlations between the different concentration levels for the calibration curve.

Uncertainty in purity of the pure styrene and uncertainty in producing standard solutions are estimated in Appendix H, Table H7. In the final uncertainty budget (Kragten spreadsheet, Appendix I) these uncertainty components are included separately because they are included in the uncertainty component of calibration curve (GC instrument).

Estimating uncertainty in molar mass

As the final link in the traceability chain in the Uncertainty Budget (Appendix H, Table H8), uncertainty in molar weights of styrene was estimated, converting mg m^{-3} to mol m^{-3} (SI units). As the final measurement result is not converted to mol m^{-3} this uncertainty component is not included in the uncertainty budget (Kragten spreadsheets, Appendix I).

DISCUSSION

According to the uncertainty budget, Appendix I, the uncertainty due to sampling and analysis on the final measurement result, **PC**, for each measurement is about 2.1% (RSD). Uncertainty due to desorption efficiency contributes with the largest part about 50% (30-70 %) to the uncertainty on each of the measurement results (PC_i). When using liquid desorption the samples are diluted in 1 ml DMF during the pre analytical step. Due to the relatively low amounts of styrene on each tube (about 1mg) samples are diluted about 1:1000 before analysis. In thermal desorption the dilution step before analysis is omitted and the uncertainty introduced on the measurement result due to desorption efficiency is eliminated. Equipment for thermal desorption is rather expensive compared to equipment for liquid desorption. The choice of method for desorption is thus dependent on an economic factor as well. For two of the measurements (Appendix I, Table I1 and I2) uncertainty in calibration of pumps is the major component to the uncertainty, about 85%. These were pumps, sampling a larger volume of air (120 ml/min) compared to the other pumps used (20-50 ml/min). To reduce contribution from this uncertainty component, more repeated measurements during calibration of pumps would be needed, for pumps sampling larger volumes.

In Figure 5 contributions from the different uncertainty components to the total uncertainty for estimating **PC** are illustrated in a diagram.

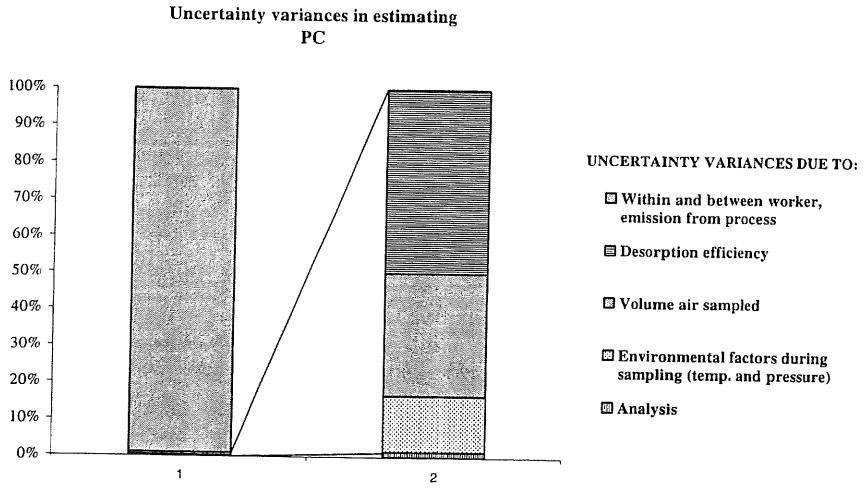


Figure 5. Contributions from uncertainty components to the total uncertainty when estimating **PC**. Column 2 is a blow-up of the lowest part of column 1.

The estimated value of the concentration of exposure to styrene in the breathing zone of a worker performing the process 'stripping' exemplified in the present paper was found to be: **PC** ± U = 294.2 mg m^{-3} ± 83.8 (U is the expanded uncertainty, coverage factor k = 2 (BIPM, 1993). RSD is about 14%.

As illustrated in Figure 5, uncertainty due to sampling (use of pumps, environmental factors and analysis (including e.g. the calibration curve for the instrument (producing standard) etc.)), accounts for absolutely minor parts of the total uncertainty. The major component to the total uncertainty, when estimating **PC** is uncertainty due to within and between worker variability and variability in emission from the process. This observation is worth noting considering the great concern analytical uncertainty commonly gets. On the other hand, analysis of a sample is the base and it is thus of great importance to validate the analytical method and to know the size of analytical uncertainty compared to sampling uncertainty, when performing occupational measurements in particular and measurements in general, to correct for possible bias. To assess the reliability of a measurement result it is of great importance to know from where the uncertainty originate.

CONCLUSIONS

The major component to the total uncertainty, when estimating **PC**, is uncertainty due to within- and between worker variability and variability in the emission from the process. Uncertainty on a single measurement (PC_i) is a minor part of the total uncertainty.

APPENDIX A - I

APPENDIX A

The Desorption Efficiency Experiment

Purpose

Values of desorption efficiency is determined by spiking solvent onto the sorbent, transferring the sorbent to a vial containing a suitable liquid for desorption (NIOSH, 1994). Styrene has previously been sampled on charcoal tubes followed by using *N,N*-dimethylformamide (DMF) as desorption liquid before analysis on GC. Compared to carbondisulfide (CS_2), which is commonly used as desorbtion liquid (NIOSH, 1994), DMF is more easy to handle and not as harmful as CS_2.

As a part of a PhD project, desorption efficiency of styrene on charcoal tubes using DMF as desorption liquid, was studied. These observations are included in Figure A1. Recovery seems to be low and highly dependent on load. Recovery was found to be about 50% for higher concentrations (800-1200 μg/ml) and about 35% for concentrations less than 200 μg/ml. A large uncertainty to the final measurement result is introduced, especially at lower concentration levels, using the method in the form described above in which extrapolation propagate the errors. The method (Johansen *et al.*, 1981) had to be improved to minimize uncertainty due to recovery.

An experiment was designed to compare desorption efficiency of the method for measuring styrene using three different adsorbents: charcoal, silica gel and Tenax combined with use of three different desorption solvents: CS_2, DMF and 2-butanone (referred to as MEK (Methyl Ethyl Ketone)), to find the best combination to obtain the highest recovery. MEK was used as the third desorption liquid due to a high degree of similar physical chemical properties with styrene. Nine concentration levels of styrene, covering the area 10 – 1200 μg/ml, were chosen to determine the recovery curve, for each combination. All levels were determined in duplicates.

Materials and methods

Tubes: SKC 100 mg charcoal tubes (Cat. No. 226-01, Lot. No. 2000), SKC 150 mg silica gel tubes (Cat. No. 226-10, Lot. No. 1838), SKC 30 mg Tenax tubes (Cat. No. 226-35, Lot. No. 1290). *Desorption fluid:* Carbon disulfide (99.9%) was purchased from Rathburn Chemicals, Scotland, UK, *N,N*-Dimethylformamide (99.9%) was purchased from Sigma-Aldrich and 2-Butanone (99.9%) was purchased from Sigma-Aldrich. *Analysis:* Gas chromatograph, autosystem XL (Perkin Elmer), equipped with a flame ionisation detector (FID) and a capillar column (Chrompack, WCOT Fused Silica (CP-Sil 8 CB), CP7452, length 25 m). Temperature: 70 - 110°C; 110 - 180°C. Injection volume: 1,0 µl. Styrene (>99%) was purchased from Merck Eurolab.

Desorption efficiency had been estimated using the NIOSH Method 1501 (NIOSH, 1994). Tubes were spiked with different concentrations of styrene, using a micropipette. Desorption in the 1 ml of desorption liquid for 24 hours, before analysed by GC-FID (1 µl injection). All injections were done in duplicates.

As CS_2 dissolved the Tenax polymer, one of the nine combinations was not possible.

Table A1. Experimental design of the Desorption Efficiency Experiment.

Tube	Liquid Carbondisulfide (CS_2)	Dimethylformamide (DMF)	2-Butanone (MEK)
Charcoal	X X	X X	X X
Silica gel	X X	X X	X X
Tenax	NP	X X	X X

NP - Combination not possible.

Results

In Figure A1, desorption curves of the combinations listed in Table A1, are shown. The combination of charcoal and DMF has a very bad recovery especially for lower concentrations. Due to the very low recovery, especially at lower concentrations, the uncertainty increases intensely. It seems as if the recovery increases for the combination charcoal and CS_2, but still it is rather bad with a high degree of uncertainty associated. 2-Butanone is not preferable in any of the combinations with the adsorbents.

Obviously the combination of silica gel and DMF is preferred due to 100 % ± 0.8 % recovery. Tenax and DMF is the second best, with recovery about 93% ± 1.3%.

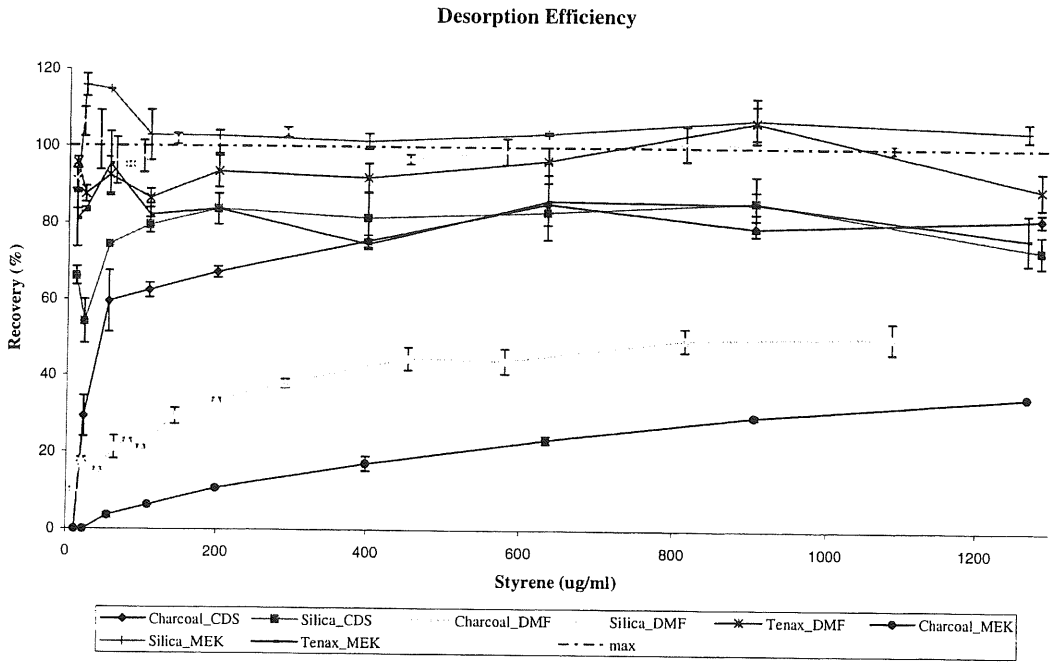


Figure A1. The Desorption Efficiency Experiment, in which desorption efficiency is determined for different combinations of adsorbent and desorption liquids

Discussion and conclusions

Previous measurements for VOCs (Volatile Organic Compounds), using the combination of silica gel and DMF had resulted in high occurrence of break through, dependent on load on tube, rate of pump flow and humidity of air, when sampling. Due to difference in physical chemical properties (difference in polarity) Tenax is expected to bind styrene more strongly compared to silica gel, but more weakly compared to charcoal. A lower degree of break through using Tenax compared to silica gel would be expected.

It was decided to reject using charcoal as adsorbent, due to the bad recovery. For measurements prospectively it was decided to use the combination of silica gel and DMF for measuring lower concentration processes (recovery 100%), and the combination of Tenax and DMF, when measuring high concentration processes to lower the occurrence of break through.

APPENDIX B

Uncertainty sources involved, when measuring styrene in air (estimating PC)

Cause-and-effect diagram

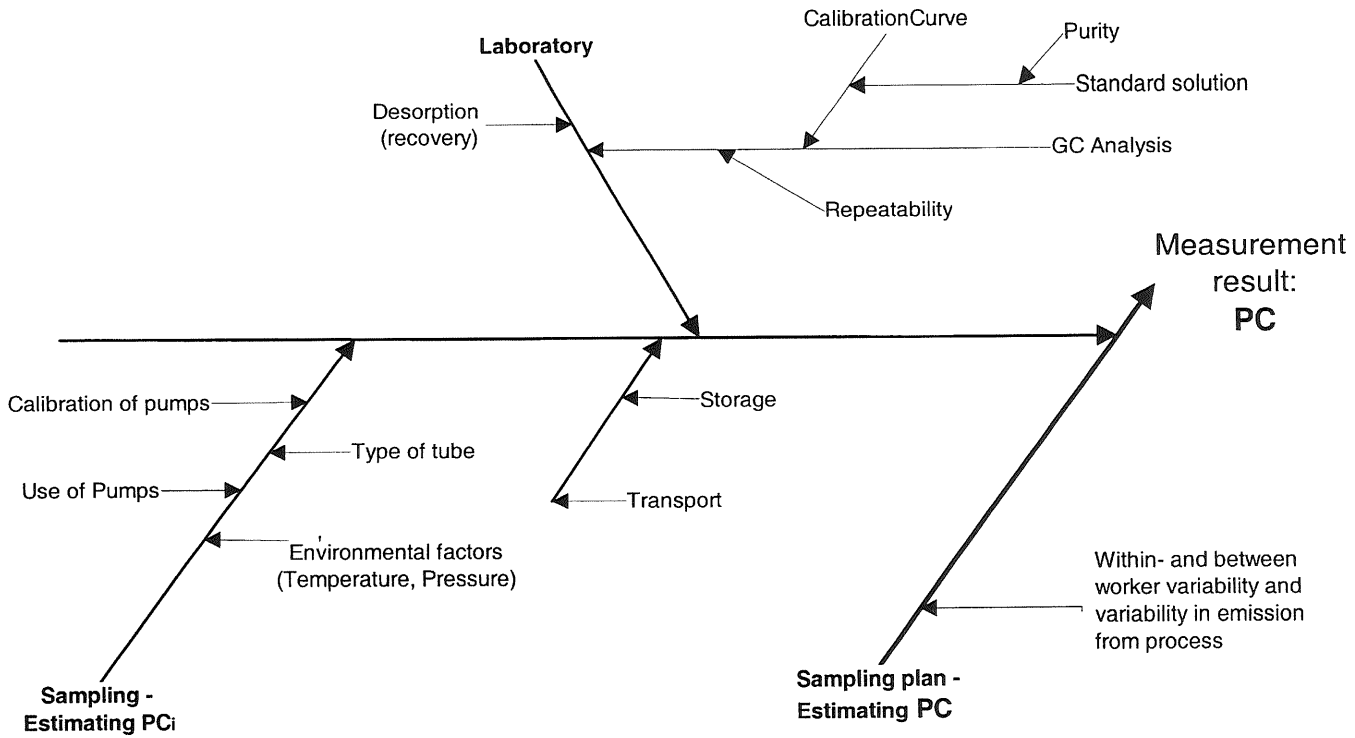


Figure B1. Cause and effect diagram of uncertainty sources in estimating PC.

APPENDIX C

The Tenax Tube Capacity Experiment

Purpose

To get an optimal method to be used for further air measurements in the occupational environment, the capacity of SKC 30 mg Tenax tubes (Cat. No. 226-35), exposed to styrene contamination was investigated. This was done by carrying out air measurements in the field, at a plant producing wings for windmills in the fibreglass reinforce plastic industry. Samples were collected using different flow rates of pump and exposure-time.

Materials and Methods

For field samples: SKC 30 mg Tenax tubes (Cat. No. 226-35, Lot. No. 1290). SKC pumps (226-03, 226-04), calibrated before and after the measurements were done. *For analytical use:* Gas chromatograph, autosystem XL (Perkin Elmer), equipped with a flame ionisation detector (FID) and a capillar column. Desorption fluid: Dimethylformamide (99.9%). Desorption efficiency had been estimated using NIOSH, Method 1501, (NIOSH, 1994).

The experimental design was set up as shown below (Table C1). It was decided to perform the measurements close to a process where the workers were exposed to a relatively high concentration of styrene during a period of about 1 hour.

The measurements performed in this experiment reflects the external air concentration in the room close to the lamination process. All workers handling this process were instructed to wear protection equipment.

All pumps were started at the same time. After about 40 minutes, half of the pumps (the first column) were stopped. The rest of the pumps (the second column) were stopped after about 80 minutes. Each sampling was carried out in duplicate. Replicates were placed in randomised order when performing the experiment to eliminate possible introduction of bias.

Results

In Table C1 the results from the analysis of the tubes are shown. The measured concentration of styrene in the air ([C]) as a mean value of two pair of tubes is shown in each cell.

The content of styrene in the control layer (CL) compared to the overall content of styrene found for each pair of Tenax tubes is expressed in percentages. The approximated amount of loss compared to expected total amount found is shown in percentage (Loss).

Table C1. Results of the Tenax Tube Capacity Experiment

Flow [ml/min]	Time [min] 40	Time [min] 80
50	1a [C] = 26.12 ± 0.043 CL = 0% Loss ~ 0%	2a [C] = 27.28 ± 1.269 CL = 3% Loss ~ 0%
120	1b [C] = 27.98 ± 1.830 CL = 7% Loss ~ 0%	2b [C] = 28.91 ± 1.494 CL = 24% Loss ~ 0%
200	1c [C] = 27.86 ± 0.374 CL = 20% Loss ~ 0%	2c [C] = 18.13 ± 1.515 CL = 26% Loss ~ 37%

Experiment no. is shown in left corner of each cell. Flow is the rate of flow for each pump [ml min^{-1}], Time is the exposure time [min], [C] is the mean value of concentration of styrene in air [mg m^{-3}], SD is the standard deviation, CL is the content of styrene in the control layer compared to the overall content of styrene found for each pair of Tenax tube, expressed in percentages, Loss is the approximated amount of styrene lost during sampling ('blown through').

Discussion

The value of [C] ought to be the same for all samples collected during the same period (40 minutes: 1a, 1b, 1c) and (80 minutes: 2a, 2b, 2c). The experiment 2a shows that the concentration of styrene in the air was almost constant during the whole period (all 80 minutes), the experiment took place. It seems as if the measured value [C] stays the same during the experiment no matter flow rate and time for sampling for most of the experiments, except from experiment 2c. In this case styrene seems to have been 'blown through' both layers leading to a loss of about 37%, probably due to the high flow rate. The capacity of the Tenax tube is exceeded in 2c.

As can be seen from CL almost no styrene was detected at the control layer, neither after 40 or 80 minutes for the pumps with a rate of 50 ml min^{-1}. The amount of styrene in the control layer increases as flow and time increases.

According to the experiments 2b and 2c the values of CL are approximately the same (about 25%), but the concentration of styrene measured in 2c is only about 2/3 times the value of 2b. This experiment shows that a limit of 25% in the control layer could be an acceptable criterion, but it does not guarantee that serious loss due to 'blown trough' can have happened.

Conclusions

According to the observations of this experiment, it can be concluded, that 50 ml min^{-1} is a useful rate of pump flow for styrene sampling (concentration of about 25 mg m^{-3}) with a maximum value for exposure time of about 1½ hours. A flow rate of 120 ml min^{-1} is acceptable as well for shorter periods (about 30 minutes). A limit for acceptance of appearance of contaminant in the control layer is suggested to be about 15%, to ensure that no loss due to blow through have happened.

APPENDIX D

The Storage Experiment

Purpose

Possible influence on samples due to storage was investigated during a period of 6 weeks. An experiment was set up with the purposes to investigate if changes due to storage at 4°C (refrigerator) or at –18 °C (freezer), were observed:

- If styrene was walking from the main layer (A) to the control layer (B) on the silica tube during storage.
- Checking if any changes in styrene concentration could be seen during storage (stability).

20 silica gel tubes were spiked on the A-layer with styrene. These were stored in refrigerator for 4 days. 10 of the spiked tubes were placed in refrigerator and 10 were placed in a freezer. 2 from each of the places were desorbed and analysed after 0, 1, 2, 3 and 6 weeks.

Materials and Methods

20 SKC 150 mg Silica gel Tubes (226-10, lot. no. 1838) were spiked in the A layer with 1200 µg styrene (1.3 µl). The tubes were stored for 4 days at 4°C. 4 tubes were desorbed (week 0) for one day in 1 ml dimethylformamide and the content of styrene at A- and B-layer was analysed on GC-FID. The rest of the tubes were stored in refrigerator and freezer for desorption and analysis the following weeks (week 1, 2, and 6).

Results

Table D1.1 The Storage Experiment. Silica gel tubes spiked with styrene (µg/ml). Storage temperature: 4°C.

Storage temperature 4°C	Week 0	Week 1	Week 2	Week 3	Week 6
1.A	1177	1192	1142	1191	1213
1.A	1176	1182	1133	1182	1212
1.B	0	0	0	0	5
1.B	0	0	0	.	5
2.A	1249	1201	1184	1166	1197
2.A	1231	1199	1187	.	1201
2.B	0	0	0	.	3
2.B	0	0	0	.	2

Table D1.2 The Storage Experiment. Silica gel tubes spiked with styrene (µg/ml). Storage temperature: -18°C.

Storage temperature -18°C	Week 0	Week 1	Week 2	Week 3	Week 6
1.A	1174	1187	1206	1145	1228
1.A	1172	1174	.	1152	1254
1.B	0	0	0	.	0
1.B	0	0	.	.	0
2.A	1104	1171	1133	1100	1162
2.A	1115	1178	1193	0043	1172
2.B	0	0	0	0	0
2.B	0	0	0	.	0

. data missing

The values fluctuate around the mean value with a variability about the same as the variability in short-term repeatability of the GC-instrument. It is thus concluded, that there is no effect due to storage during the 6 weeks period. Neither due to styrene walking from A- to B-layer or changes in the styrene concentrations observed in general. There is no contribution to the total uncertainty due to storage.

APPENDIX E

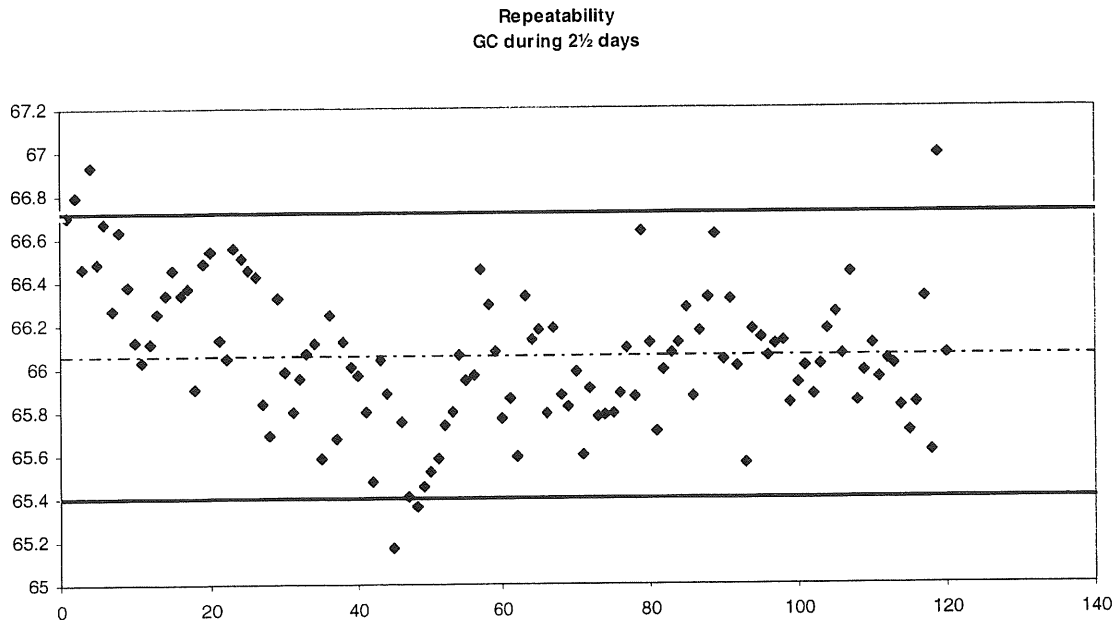


Figure E1 Short-term repeatability of the gas chromatograph during a period of 2½ days.
Data are sorted in time order.

- on the following page

Figure E2 (from WinAMIQAS). Westgard plot of the repeatability of the gas chromatograph.
Long-term variation during a period of 5 months.
IHRM of styrene in DMF in two concentration levels were used: a) 912 µg/ml and b) 61.5 µg/ml.

Westgard Chart report

WinAMIQAS report **Version 1.12**

Printed: 9. July 2002

Project Title: styren **Project ID:** 1

Journal No:

Matrix name: Dimethylformamide

Measurand name: Styrene

Method name: gc-fid

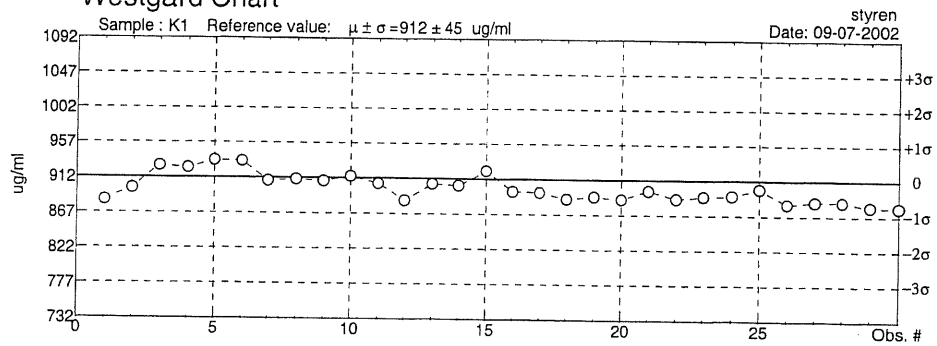
Units: ug/ml

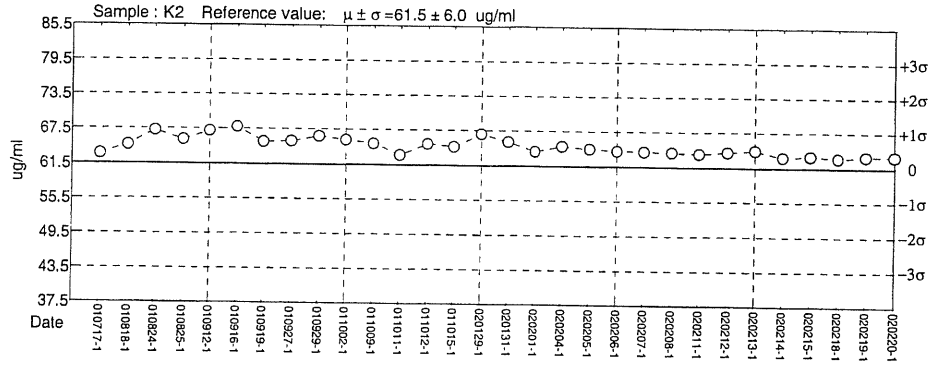
Comment:

Sample 1:		
ID:	K1	**(used)**
Ref. value:	912	912
Std. dev:	45	45

Sample 2:		
ID:	K2	**(used)**
Ref. value:	61.5	61.5
Std. dev:	6	6

Westgard Chart





Values are: True

Date & initials

Signature

APPENDIX F

Certificate of Analysis

MERCK

http://certificates.merck.de

Date of print: *08.05.2002*

8.07679.0000 **STYRENE (STABILISED) FOR SYNTHESIS**

Batch **S31290**

Assay [GC, area%]	99.9%
Density [d 20°/4°]	0.906
Identity [IR]	conforms
Date of examination:	22.01.2001
minimum shelf life:	17.01.2002

Dr. Bolkart Tel. (08102) 802-167
Analytical department Dr. Th. Schuchardt & Co.

This document has been produced electronically and is valid without a signature.

Merck Schuchardt OHG, D-85662 Hohenbrunn **Page1 / 1**

MS000051062EN Anl: 5614110

Figure F1. Certificate from supplier of the purity of the styrene

APPENDIX G

- on following pages

Figure G1. Mass spectrum of styrene used

RUN SUMMARY: data/02CKWsvampe/02svam0020

ACQUISITION INFORMATION:

Instrument Name	: Profile
Created	: 11-Mar-2002 11:31
Mass Range	: 29 - 418
Scan rate	: 0.4 seconds per decade.
Experiment Type	: ~~HRP~~ LRP
Resolution	: 600
Acquisition Time	: 19:38
Collision Gas	:
Activation Method	: Electron Beam
Interscan Time	: 501.6 ms
Source Temperature	: 150 Deg C
Ion Potential	: 4000 V
Ion Beam Energy	: 70 eV
Sampling Rate	: 14 us
Autozero Samples	: 0
Mass defect	: 0.50 amu
Stabilisation	: Current

RUN TITLE:

Headspace over STYRENE Merck 807679
Styrene

DF : 0.25 µm.

GC 60 m Sil 19 0.32 mm 20/4-250-15
ATD ovn 250'C i 20 min trap med Tenax -30>300'C i 2 min
Valve og transfer 225'C tryk 7.3 psi He
Outlet split 15.11 ml/min
Desorb Flow 32.5

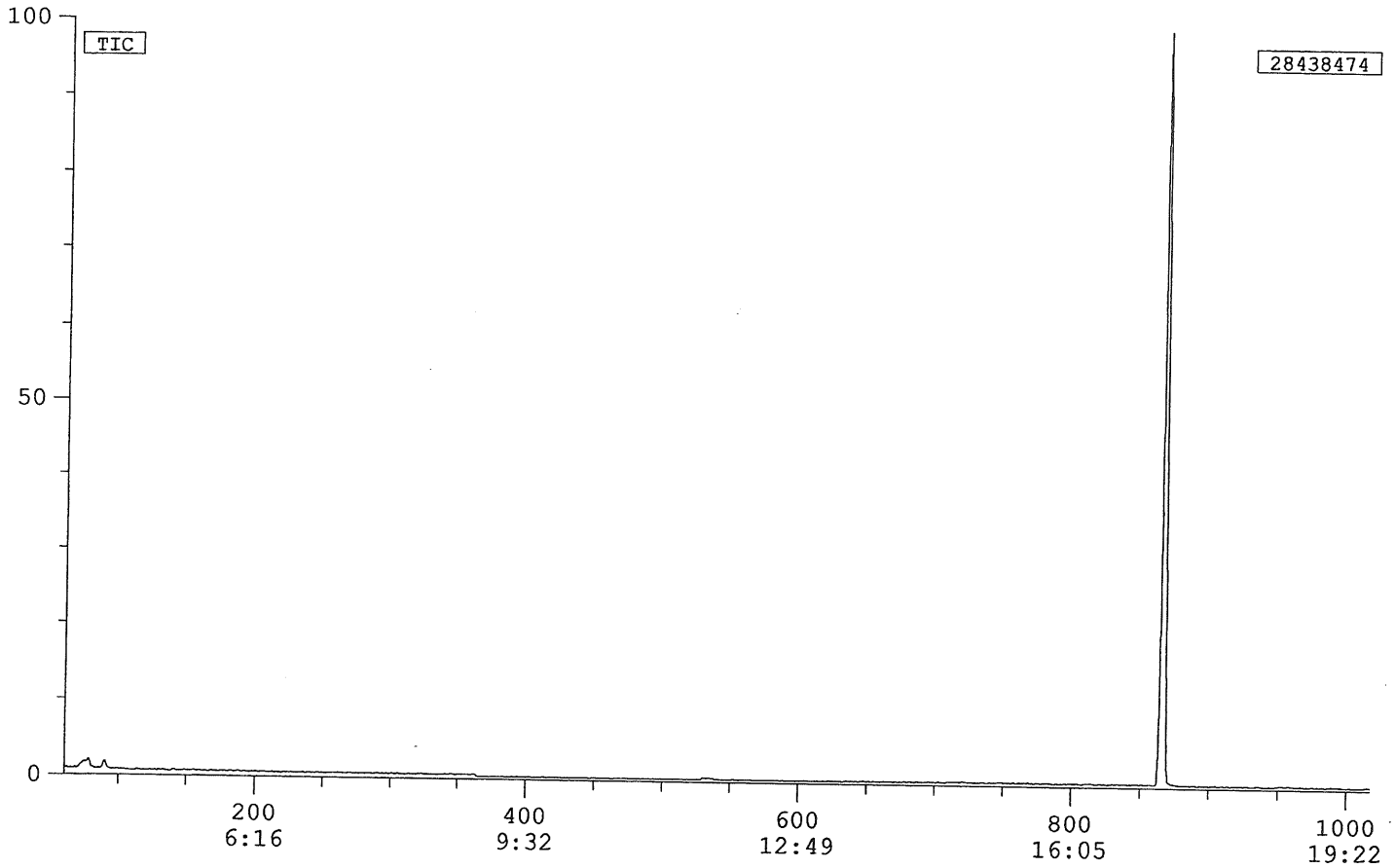
gain 415

SCAN INFORMATION:
1018 Scans of Acquired Nominal data.

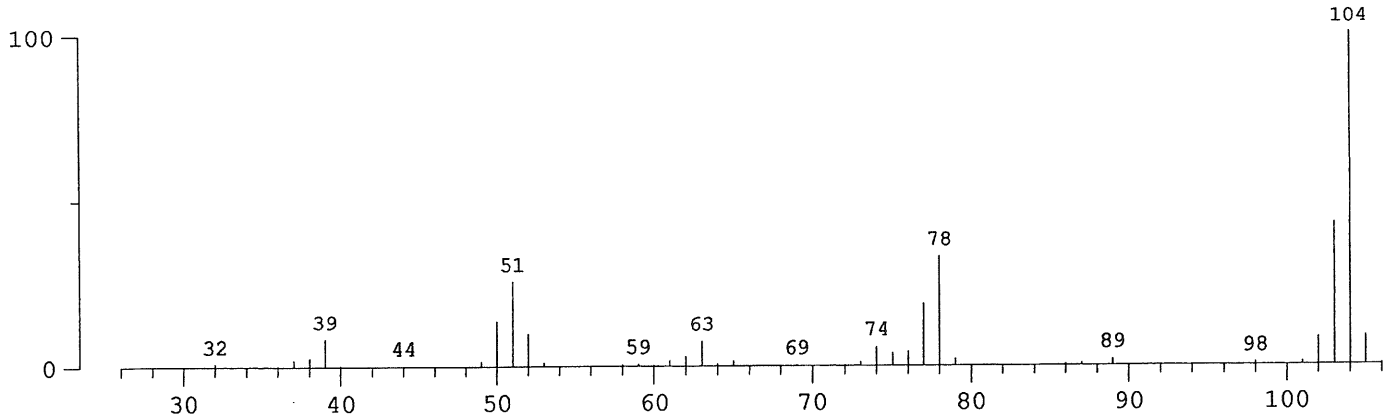
****

Runname : 02svam0020 Acquired Nominal.
This is unsmoothed data
Headspace over STYRENE Merck 807679

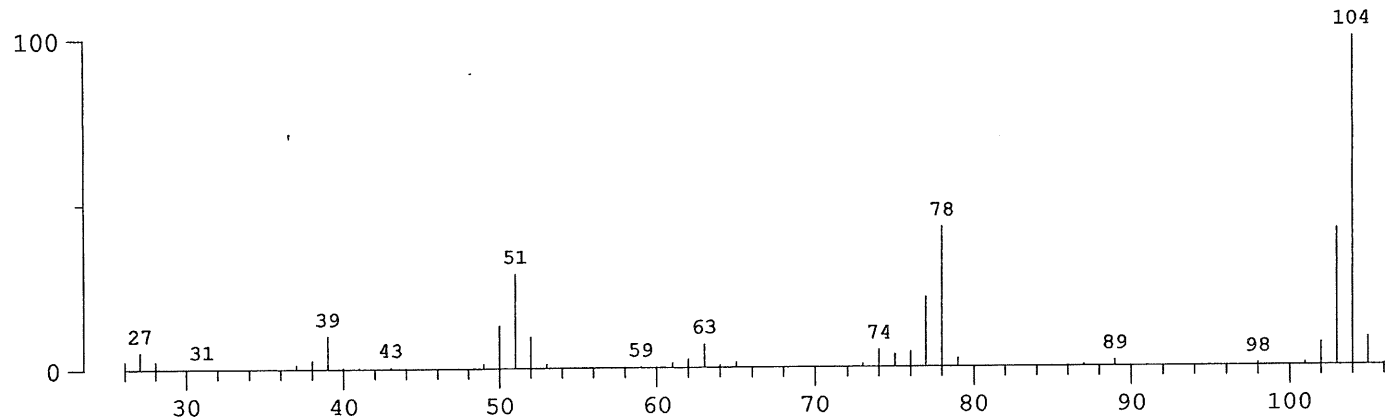
11-Mar-2002 11:31



Run=02svam0020 Scan=866 100%=8922298 ADC Mass Range=29-137
11-Mar-2002 11:31 HRP +EI Headspace over STYRENE Merck 807679



wileynbs: 69138 Rel(sim): 99 Rel(same): 81
Styrene
C8 H8 MW=104.062600 CAS=100425



APPENDIX H

Table H1. Estimation of uncertainty of estimating process concentration and air sampled

#	Input Quantity	Symbol (x_i)	Value of input estimate	Unit	Degrees of freedom	Uncertainty	Type of uncertainty (A/B)	Type of distribution	Standard uncertainty $u(x_i)$	Relative standard uncertainty (%)	Reference
1	Within and between Worker	$\overline{D}$	0	mg/m3	11	41.81	A	Normal	41.81	-	Repeated measure-ments
2	Homogeneity of air in breathing zone	δ_S	0	mg/m3	-	-	-	-	-	-	Repeated measure-ments

Table H2. Estimation of uncertainty of use of pumps in field and drift

#	Input Quantity	Symbol (x_i)	Value of input estimate	Unit	Degrees of freedom	Uncertainty	Type of uncertainty (A/B)	Type of distribution	Standard uncertainty $u(x_i)$	Relative standard uncertainty (%)	Reference
3	Reading pumps in field – start	Counter start	*Value acc. to Appendix I*	Count	-	1	B	Rectangular	$\frac{1}{\sqrt{3}}$		Own estimate
4	Reading pumps in field – stop	Counter stop	*Value acc. to Appendix I*	Count	-	1	B	Rectangular	$\frac{1}{\sqrt{3}}$		Own estimate
5	Drift	d_r	0	ml/sec	-	0	A	Normal	0	-	Repeated measure-ments

Table H3. Estimation of uncertainty due to transport and storage

#	Input Quantity	Symbol (x_i)	Value of input estimate	Unit	Degrees of freedom	Uncertainty	Type of uncertainty (A/B)	Type of distribution	Standard uncertainty $u(x_i)$	Relative standard deviation (%)	Reference
6	Transport Refrigerator		0	-	-	0	-	-	0	-	Repeated measure-ments
7	Storage Breakthrough		0	-	-	0	-	-	0	-	Repeated measure-ments
8	Storage Loss		0	-	-	0	-	-	0	-	Repeated measure-ments

Table H4. Estimation of uncertainty in pre analytical handling (desorption)

#	Input Quantity	Symbol (x_i)	Value of input estimate	Unit	Degrees of freedom	Uncertainty	Type of uncertainty (A/B)	Type of distribution	Standard uncertainty $u(x_i)$	Relative standard deviation (%)	Reference
9	Desorption Tenax	D_T	*Value acc. to Table H6*	-		*Value acc. to Table H6*	A	normal	*Value acc. to Table H6*		Repeated measure-ments
10	Desorption Silica gel	D_S	*Value acc. to Table H6*	-		*Value acc. to Table H6*	A	normal	*Value acc. to Table H6*		Repeated measure-ments

Table H5. Estimation of uncertainty in using instrument for analysis (GC). *For validation purposes only.*

#	Input quantity	Symbol (x_i)	Value of input estimate	Unit	Degrees of freedom	Uncertainty	Type of uncertainty (A/B)	Type of distribution	Standard uncertainty $u(x_i)$	Relative standard deviation (%)	Reference
11	Repeatability Double injections	R_{inj}	66.1	µg/ml	59	0.10	A	Normal	0.10	0.15	Repeated measure-ments
12	Repeatability Short term effects (2½day)	R_{st}	66.0	µg/ml	59	0.29	A	Normal	0.29	0.44*	Repeated measure-ments
13	Repeatability Long term effects (5 months)	R_{lt}	64.8	µg/ml	29	1.19	A	Normal	1.19	1.8	Repeated measure-ments
			899.4	µg/ml	29	16	A	Normal	16	1.8	

*used for estimation of SD (repeatability) for 'Area, C1' and 'Area, C2' in the uncertainty budget (Appendix I)

Table H6. Estimation of uncertainty in calibrations (calibration of instrument (GC), desorption (recovery) and pumps)

#	Input quantity	Symbol (x_i)	Value of input estimate	Unit	Degrees of freedom	Uncertainty	Type of uncertainty (A/B)	Type of distribution	Standard uncertainty $u(x_i)$	Relative standard deviation (%)	Reference
14	*Instrument* Calibration curve – intercept	A	-582.42	-	-	35.0	A	Normal	35.0	6.0	Repeated measure-ments
15	Calibration curve – slope	B	882.12	-	-	2.8	A	Normal	2.8	0.32	Repeated measure-ments
16	*Determining Desorption Efficiency*										Repeated measure-ments
	Calibration for recovery loss Tenax tube	DE_T	93	-	23	6.0	A	normal	1.22	1.31	
17	Calibration for recovery loss Silica gel tube	DE_S	100	-	23	3.9	A	normal	0.80	0.80	Repeated measure-ments
3	Calibration of pumps Volume soap bobble flow meter	V_{bf}	46.1	Ml	11	0.54	A	Normal	0.16	0.35	Repeated measure-ments
18	Counter start	Counter Start	*Value acc. to Appendix I*	Count	-	1	B	Rectangular	$\frac{1}{\sqrt{3}}$		Own estimate
19	Counter stop	Counter Stop	*Value acc. to Appendix I*	Count	-	1	B	Rectangular	$\frac{1}{\sqrt{3}}$		Own estimate

Table H7. Estimation of uncertainty in purity of styrene and production of standards. *Used for validation.*

#	Input quantity	Symbol (x_i)	Value of input estimate	Unit	Degrees of freedom	Uncertainty	Type of uncertainty (A/B)	Type of distribution	Standard uncertainty $u(x_i)$	Relative standard deviation (%)	Reference
20	Purity of styrene		99.9	%	-	0.1	B	Rectangular	$\frac{0.1}{\sqrt{3}} = 0.06$	0.06	Suppliers certificate
21	Weighting	W	95	mg	-	0.015	B	Rectangular	$\frac{0.015}{\sqrt{3}}$	0.009	Instrument specification/ Own estimate
22	Dilution		100	ml	-	0.2	B	Rectangular	$\frac{0.2}{\sqrt{3}}$	0.12	Suppliers specification

Table H8. Estimation of uncertainty in molar mass. *Used for validation.*

#	Input quantity	Symbol (x_i)	Value of input estimate	Unit	Degrees of freedom	Uncertainty	Type of uncertainty (A/B)	Type of distribution	Standard uncertainty $u(x_i)$	Relative standard deviation	Reference
24	Molar mass (C_8H_8)	M_W	104.15	g mol^{-1}	-	$\sqrt{8\left(\frac{0.001}{\sqrt{3}}\right)^2 + 8\left(\frac{0.0001}{\sqrt{3}}\right)^2}$	B	Rectangular	0.0009	$8.9\ 10^{-4}$	Handbook of Chemistry and Physics

APPENDIX I (p.1-13)

Table I 1 – Table I 12. Uncertainty budgets for estimating uncertainties of each PC_i, using the spreadsheet method (Kragten, 1994), (EURACHEM, 2000).

Table I 13. Estimation of uncertainty of estimating **PC**.

Table I1

PC_1: tube S657 (S656 missing)

		Area, C1	Area, C2	a	b	Count,stopC1	Count,startC1	Count,stopC2	Count,startC2	f, C1	f, C2	DE	t	P
		858633	0	-582.42	882.12	45036	41716	0	0	0.5281	0	100	21	1003
		3777.9852	0	35	2.8	1	1	0	0	0.0176	0	0.8	1	5
Area, C1	858633	862410.99	858633	858633	858633	858633	858633	858633	858633	858633	858633	858633	858633	858633
Area, C2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a	-582.42	-582.42	-582.42	-547.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42
b	882.12	882.12	882.12	882.12	884.92	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12
Count,stopC1	45036	45036	45036	45036	45036	45037	45036	45036	45036	45036	45036	45036	45036	45036
Count,startC1	41716	41716	41716	41716	41716	41716	41717	41716	41716	41716	41716	41716	41716	41716
Count,stopC2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Count,startC2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
f, C1	0.5281	0.5281	0.5281	0.5281	0.5281	0.5281	0.5281	0.5281	0.5281	0.5457	0.5281	0.5281	0.5281	0.5281
f, C2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DE	100	100	100	100	100	100	100	100	100	100	100	100.8	100	100
t	21	21	21	21	21	21	21	21	21	21	21	21	22	21
P	1003	1003	1003	1003	1003	1003	1003	1003	1003	1003	1003	1003	1003	1008
	557.29388	559.74431	557.29388	557.27118	555.5305	557.1260715	557.4617907	557.2938805	557.2938805	539.3199529	557.29388	552.87091	559.18944	554.52953
		2.4504309	0	-0.022701	-1.763349	-0.167809058	0.167910178	0	0	-17.97392761	0	-4.4229673	1.8955574	-2.7643546
		6.0046117	0	0.0005153	3.1094	0.02815988	0.028193828	0	0	323.0620738	0	19.56264	3.5931379	7.6416562
	19.053356													
RSD	0.0341891													
		0.0165402	0	1.42E-06	0.008565	7.75689E-05	7.76624E-05	0	0	0.889903667	0	0.0538871	0.0098976	0.0210496

Table I2

PC_2: tube S680 (S681 missing)

		Area, C1	Area, C2	a	b	Count,stopC1	Count,startC1	Count,stopC2	Count,startC2	f, C1	f, C2	DE	t	P
		681140	0	-582.42	882.12	365031	360190	0	0	0.5518	0	100	21	1003
		2997.016	0	35	2.8	1	1	0	0	0.0137	0	0.8	1	5
Area, C1	681140	684137.02	681140	681140	681140	681140	681140	681140	681140	681140	681140	681140	681140	681140
Area, C2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a	-582.42	-582.42	-582.42	-547.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42
b	882.12	882.12	882.12	882.12	884.92	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12
Count,stopC1	365031	365031	365031	365031	365031	365032	365031	365031	365031	365031	365031	365031	365031	365031
Count,startC1	360190	360190	360190	360190	360190	360190	360191	360190	360190	360190	360190	360190	360190	360190
Count,stopC2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Count,startC2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
f, C1	0.5518	0.5518	0.5518	0.5518	0.5518	0.5518	0.5518	0.5518	0.5518	0.5655	0.5518	0.5518	0.5518	0.5518
f, C2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DE	100	100	100	100	100	100	100	100	100	100	100	100.8	100	100
t	21	21	21	21	21	21	21	21	21	21	21	21	22	21
P	1003	1003	1003	1003	1003	1003	1003	1003	1003	1003	1003	1003	1003	1008
	290.21995	291.49583	290.21995	290.20505	289.3017	290.1600107	290.2799116	290.2199488	290.2199488	283.1889792	290.21995	287.91662	291.20709	288.78037
		1.2758768	0	-0.0149	-0.918293	-0.059938032	0.059962799	0	0	-7.030969581	0	-2.3033329	0.9871427	-1.4395831
		1.6278616	0	0.000222	0.843262	0.003592568	0.003595537	0	0	49.43453325	0	5.3053426	0.9744507	2.0723994
	7.7630703													
RSD	0.0267489													
		0.0270116	0	3.684E-06	0.013993	5.96126E-05	5.96619E-05	0	0	0.820282422	0	0.0880332	0.0161694	0.034388

Table I3
PC_3: tube S922/S923

		Area, C1	Area, C2	a	b	Count,stopC1	Count,startC1	Count,stopC2	Count,startC2	f, C1	f, C2	DE	t	P
		141838.5	139808.5	-582.42	882.12	785542	784447	877863	876866	0.4971	0.5154	100	23	1006
		624.0894	615.1574	35	2.8	1	1	1	1	0.0034	0.0012	0.8	1	5
Area, C1	141838.5	142462.59	141838.5	141838.5	141838.5	141838.5	141838.5	141838.5	141838.5	141838.5	141838.5	141838.5	141838.5	141838.5
Area, C2	139808.5	139808.5	140423.66	139808.5	139808.5	139808.5	139808.5	139808.5	139808.5	139808.5	139808.5	139808.5	139808.5	139808.5
a	-582.42	-582.42	-582.42	-547.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42
b	882.12	882.12	882.12	882.12	884.92	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12
Count,stopC1	785542	785542	785542	785542	785542	785543	785542	785542	785542	785542	785542	785542	785542	785542
Count,startC1	784447	784447	784447	784447	784447	784447	784448	784447	784447	784447	784447	784447	784447	784447
Count,stopC2	877863	877863	877863	877863	877863	877863	877863	877864	877863	877863	877863	877863	877863	877863
Count,startC2	876866	876866	876866	876866	876866	876866	876866	876866	876867	876866	876866	876866	876866	876866
f, C1	0.4971	0.4971	0.4971	0.4971	0.4971	0.4971	0.4971	0.4971	0.4971	0.5005	0.4971	0.4971	0.4971	0.4971
f, C2	0.5154	0.5154	0.5154	0.5154	0.5154	0.5154	0.5154	0.5154	0.5154	0.5154	0.5166	0.5154	0.5154	0.5154
DE	100	100	100	100	100	100	100	100	100	100	100	100.8	100	100
t	23	23	23	23	23	23	23	23	23	23	23	23	24	23
P	1006	1006	1006	1006	1006	1006	1006	1006	1006	1006	1006	1006	1006	1011
	305.27625	305.93065	305.95953	305.20067	304.3103	305.13999	305.4127533	305.1199962	305.4328119	304.2617647	304.91402	302.85342	306.30759	303.76647
		0.6543991	0.6832828	-0.075576	-0.965933	-0.136257103	0.136506202	-0.156250964	0.156564721	-1.014482454	-0.3622264	-2.4228274	1.0313387	-1.5097737
		0.4282382	0.4668754	0.0057117	0.933027	0.018565998	0.018633943	0.024414364	0.024512512	1.029174649	0.131208	5.8700924	1.0636595	2.2794167
	3.5062131													
RSD	0.0114854													
		0.0348344	0.0379773	0.0004646	0.075896	0.001510225	0.001515752	0.001985952	0.001993936	0.083716772	0.0106729	0.4774945	0.0865219	0.185416

Table I4

PC_4: tube S930/S931

		Area, C1	Area, C2	a	b	Count,stopC1	Count,startC1	Count,stopC2	Count,startC2	f, C1	f, C2	DE	t	P
		180796	178572	-582.42	882.12	788282	786869	880331	879059	0.4971	0.5154	100	23	1006
		795.5024	785.7168	35	2.8	1	1	1	1	0.0034	0.0012	0.8	1	5
Area, C1	180796	181591.5	180796	180796	180796	180796	180796	180796	180796	180796	180796	180796	180796	180796
Area, C2	178572	178572	179357.72	178572	178572	178572	178572	178572	178572	178572	178572	178572	178572	178572
a	-582.42	-582.42	-582.42	-547.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42
b	882.12	882.12	882.12	882.12	884.92	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12
Count,stopC1	788282	788282	788282	788282	788282	788283	788282	788282	788282	788282	788282	788282	788282	788282
Count,startC1	786869	786869	786869	786869	786869	786869	786870	786869	786869	786869	786869	786869	786869	786869
Count,stopC2	880331	880331	880331	880331	880331	880331	880331	880332	880331	880331	880331	880331	880331	880331
Count,startC2	879059	879059	879059	879059	879059	879059	879059	879059	879060	879059	879059	879059	879059	879059
f, C1	0.4971	0.4971	0.4971	0.4971	0.4971	0.4971	0.4971	0.4971	0.4971	0.5005	0.4971	0.4971	0.4971	0.4971
f, C2	0.5154	0.5154	0.5154	0.5154	0.5154	0.5154	0.5154	0.5154	0.5154	0.5154	0.5166	0.5154	0.5154	0.5154
DE	100	100	100	100	100	100	100	100	100	100	100	100.8	100	100
t	23	23	23	23	23	23	23	23	23	23	23	23	24	23
P	1006	1006	1006	1006	1006	1006	1006	1006	1006	1006	1006	1006	1006	1011
	303.3582	304.00462	304.04226	303.29929	302.3983	303.2539717	303.4625847	303.2356803	303.4809212	302.3569871	302.9959	300.9506	304.38306	301.85792
		0.6464119	0.6840507	-0.058912	-0.959864	-0.104232722	0.104380361	-0.122524065	0.122716865	-1.001217253	-0.3623069	-2.4076048	1.0248588	-1.5002879
		0.4178484	0.4679254	0.0034706	0.921339	0.01086446	0.01089526	0.015012147	0.015059429	1.002435988	0.1312663	5.7965609	1.0503356	2.2508636
	3.4776252													
RSD	0.0114638													
		0.0345504	0.0386911	0.000287	0.076182	0.000898344	0.000900891	0.001241301	0.001245211	0.082887892	0.0108539	0.4792971	0.0868485	0.186116

Table I5
PC_5: tube T18/T19

		Area, C1	Area, C2	a	b	Count,stopC1	Count,startC1	Count,stopC2	Count,startC2	f, C1	f, C2	DE	t	P
		134489.5	148567	-582.42	882.12	257450	255045	549994	547683	0.4886	0.5632	93	21	1012
		591.7538	653.6948	35	2.8	1	1	1	1	0.0103	0.0089	1.22	1	5
Area, C1	134489.5	135081.25	134489.5	134489.5	134489.5	134489.5	134489.5	134489.5	134489.5	134489.5	134489.5	134489.5	134489.5	134489.5
Area, C2	148567	148567	149220.69	148567	148567	148567	148567	148567	148567	148567	148567	148567	148567	148567
a	-582.42	-582.42	-582.42	-547.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42
b	882.12	882.12	882.12	882.12	884.92	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12
Count,stopC1	257450	257450	257450	257450	257450	257451	257450	257450	257450	257450	257450	257450	257450	257450
Count,startC1	255045	255045	255045	255045	255045	255045	255046	255045	255045	255045	255045	255045	255045	255045
Count,stopC2	549994	549994	549994	549994	549994	549994	549994	549995	549994	549994	549994	549994	549994	549994
Count,startC2	547683	547683	547683	547683	547683	547683	547683	547683	547684	547683	547683	547683	547683	547683
f, C1	0.4886	0.4886	0.4886	0.4886	0.4886	0.4886	0.4886	0.4886	0.4886	0.4989	0.4886	0.4886	0.4886	0.4886
f, C2	0.5632	0.5632	0.5632	0.5632	0.5632	0.5632	0.5632	0.5632	0.5632	0.5632	0.5721	0.5632	0.5632	0.5632
DE	93	93	93	93	93	93	93	93	93	93	93	94.22	93	93
t	21	21	21	21	21	21	21	21	21	21	21	21	22	21
P	1012	1012	1012	1012	1012	1012	1012	1012	1012	1012	1012	1012	1012	1017
	139.09202	139.39717	139.39635	139.05767	138.6519	139.0630667	139.1209903	139.0619824	139.1220766	137.6539989	138.01177	137.29099	139.56512	138.40818
		0.3051522	0.3043381	-0.034343	-0.440105	-0.028949752	0.028973837	-0.030034132	0.030060136	-1.438017562	-1.0802418	-1.8010217	0.4731021	-0.6838349
		0.0931178	0.0926217	0.0011795	0.193692	0.000838088	0.000839483	0.000902049	0.000903612	2.067894508	1.1669223	3.243679	0.2238256	0.4676302
	2.7484625													
RSD	0.01976													
		0.0123269	0.0122612	0.0001561	0.025641	0.000110946	0.00011113	0.000119413	0.00011962	0.273746607	0.1544765	0.4293962	0.0296299	0.0619046

Table I6
PC_6: tube S882/S883

		Area, C1	Area, C2	a	b	Count,stopC1	Count,startC1	Count,stopC2	Count,startC2	f, C1	f, C2	DE	t	P
		21905.5	35459	-582.42	882.12	409043	408751	720179	719797	0.3782	0.43	100	22	1009
		96.3842	156.0196	35	2.8	1	1	1	1	0.0021	0.0021	0.8	1	5
Area, C1	21905.5	22001.884	21905.5	21905.5	21905.5	21905.5	21905.5	21905.5	21905.5	21905.5	21905.5	21905.5	21905.5	21905.5
Area, C2	35459	35459	35615.02	35459	35459	35459	35459	35459	35459	35459	35459	35459	35459	35459
a	-582.42	-582.42	-582.42	-547.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42
b	882.12	882.12	882.12	882.12	884.92	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12
Count,stopC1	409043	409043	409043	409043	409043	409044	409043	409043	409043	409043	409043	409043	409043	409043
Count,startC1	408751	408751	408751	408751	408751	408751	408752	408751	408751	408751	408751	408751	408751	408751
Count,stopC2	720179	720179	720179	720179	720179	720179	720179	720180	720179	720179	720179	720179	720179	720179
Count,startC2	719797	719797	719797	719797	719797	719797	719797	719797	719798	719797	719797	719797	719797	719797
f, C1	0.3782	0.3782	0.3782	0.3782	0.3782	0.3782	0.3782	0.3782	0.3782	0.3803	0.3782	0.3782	0.3782	0.3782
f, C2	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.4321	0.43	0.43	0.43
DE	100	100	100	100	100	100	100	100	100	100	100	100.8	100	100
t	22	22	22	22	22	22	22	22	22	22	22	22	23	22
P	1009	1009	1009	1009	1009	1009	1009	1009	1009	1009	1009	1009	1009	1014
	239.92801	240.423	240.4667	239.62742	239.1688	239.5338545	240.3248756	239.6031012	240.2546255	239.2902924	239.32323	238.02382	240.74133	238.74493
		0.4949854	0.5386892	-0.300589	-0.759163	-0.394156063	0.396865039	-0.324909358	0.326614919	-0.637718184	-0.6047781	-1.9041906	0.8133153	-1.183077
		0.2450105	0.290186	0.0903535	0.576328	0.155359002	0.157501859	0.105566091	0.106677306	0.406684482	0.3657565	3.6259417	0.6614818	1.3996711
	2.8612092													
RSD	0.0119253													
		0.0299285	0.0354468	0.0110369	0.0704	0.018977421	0.019239175	0.012895115	0.013030852	0.049677344	0.0446779	0.4429162	0.0808014	0.1709727

Table I7

PC_7: tube S1031/S1032

		Area, C1	Area, C2	a	b	Count,stopC1	Count,startC1	Count,stopC2	Count,startC2	f, C1	f, C2	DE	t	P
		54516	53161	-582.42	882.12	806619	805609	897321	896398	0.4883	0.5127	100	21	1030
		239.8704	233.9084	35	2.8	1	1	1	1	0.0035	0.0064	0.8	1	5
Area, C1	54516	54755.87	54516	54516	54516	54516	54516	54516	54516	54516	54516	54516	54516	54516
Area, C2	53161	53161	53394.908	53161	53161	53161	53161	53161	53161	53161	53161	53161	53161	53161
a	-582.42	-582.42	-582.42	-547.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42
b	882.12	882.12	882.12	882.12	884.92	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12
Count,stopC1	806619	806619	806619	806619	806619	806620	806619	806619	806619	806619	806619	806619	806619	806619
Count,startC1	805609	805609	805609	805609	805609	805609	805610	805609	805609	805609	805609	805609	805609	805609
Count,stopC2	897321	897321	897321	897321	897321	897321	897321	897322	897321	897321	897321	897321	897321	897321
Count,startC2	896398	896398	896398	896398	896398	896398	896398	896398	896399	896398	896398	896398	896398	896398
f, C1	0.4883	0.4883	0.4883	0.4883	0.4883	0.4883	0.4883	0.4883	0.4883	0.4918	0.4883	0.4883	0.4883	0.4883
f, C2	0.5127	0.5127	0.5127	0.5127	0.5127	0.5127	0.5127	0.5127	0.5127	0.5127	0.5191	0.5127	0.5127	0.5127
DE	100	100	100	100	100	100	100	100	100	100	100	100.8	100	100
t	21	21	21	21	21	21	21	21	21	21	21	21	22	21
P	1030	1030	1030	1030	1030	1030	1030	1030	1030	1030	1030	1030	1030	1035
	124.74136	125.01066	125.01504	124.66111	124.3467	124.6801712	124.802664	124.6733022	124.8095593	124.3011258	123.96608	123.75135	125.16565	124.13874
		0.2693015	0.273685	-0.080246	-0.394698	-0.061185719	0.061306999	-0.068054757	0.068202381	-0.440231123	-0.7752815	-0.9900108	0.4242903	-0.6026153
		0.0725233	0.0749035	0.0064394	0.155786	0.003743692	0.003758548	0.00463145	0.004651565	0.193803442	0.6010614	0.9801213	0.1800223	0.3631451
	1.6262199													
RSD	0.0130367													
		0.0274233	0.0283233	0.002435	0.058907	0.001415603	0.001421221	0.001751291	0.001758897	0.073282949	0.2272795	0.3706135	0.0680719	0.1373162

Table I8

PC_8: tube S1251/S1252

		Area, C1	Area, C2	a	b	Count,stopC1	Count,startC1	Count,stopC2	Count,startC2	f, C1	f, C2	DE	t	P
		34470	32732	-582.42	882.12	819334	819006	908863	908573	0.4936	0.5127	100	22	1033
		151.668	144.0208	35	2.8	1	1	1	1	0.0054	0.0064	0.8	1	5
Area, C1	34470	34621.668	34470	34470	34470	34470	34470	34470	34470	34470	34470	34470	34470	34470
Area, C2	32732	32732	32876.021	32732	32732	32732	32732	32732	32732	32732	32732	32732	32732	32732
a	-582.42	-582.42	-582.42	-547.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42
b	882.12	882.12	882.12	882.12	884.92	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12
Count,stopC1	819334	819334	819334	819334	819334	819335	819334	819334	819334	819334	819334	819334	819334	819334
Count,startC1	819006	819006	819006	819006	819006	819006	819007	819006	819006	819006	819006	819006	819006	819006
Count,stopC2	908863	908863	908863	908863	908863	908863	908863	908864	908863	908863	908863	908863	908863	908863
Count,startC2	908573	908573	908573	908573	908573	908573	908573	908573	908574	908573	908573	908573	908573	908573
f, C1	0.494	0.494	0.494	0.494	0.494	0.494	0.494	0.494	0.494	0.4994	0.494	0.494	0.494	0.494
f, C2	0.513	0.513	0.513	0.513	0.513	0.513	0.513	0.513	0.513	0.513	0.5194	0.513	0.513	0.513
DE	100	100	100	100	100	100	100	100	100	100	100	100.8	100	100
t	22	22	22	22	22	22	22	22	22	22	22	22	23	22
P	1033	1033	1033	1033	1033	1033	1033	1033	1033	1033	1033	1033	1033	1038
	243.88976	244.40829	244.42604	243.63977	243.1181	243.525508	244.2562418	243.4634705	244.3190016	242.5939424	242.36122	241.95413	244.71651	242.71495
		0.5185312	0.53628	-0.249987	-0.771698	-0.364252952	0.366480799	-0.426290514	0.429240622	-1.295818573	-1.5285396	-1.935633	0.826745	-1.1748062
		0.2688747	0.2875963	0.0624935	0.595518	0.132680213	0.134308176	0.181723603	0.184247511	1.679145773	2.3364332	3.7466752	0.6835072	1.3801695
	3.4166319													
RSD	0.0140089													
		0.0230332	0.0246369	0.0053535	0.051015	0.011366056	0.011505515	0.01556736	0.015783571	0.143844091	0.2001506	0.3209591	0.0585527	0.1182323

Table I9

PC_9: tube T169

		Area, C1	Area, C2	a	b	Count,stopC1	Count,startC1	Count,stopC2	Count,startC2	f, C1	f, C2	DE	t	P
		22066.5	0	-582.42	882.12	122409	122250	0	0	0.4487	0	93	21	1033
		97.0926	0	35	2.8	1	1	0	0	0.0067	0	1.22	1	5
Area, C1	22066.5	22163.593	22066.5	22066.5	22066.5	22066.5	22066.5	22066.5	22066.5	22066.5	22066.5	22066.5	22066.5	22066.5
Area, C2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
a	-582.42	-582.42	-582.42	-547.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42
b	882.12	882.12	882.12	882.12	884.92	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12
Count,stopC1	122409	122409	122409	122409	122409	122410	122409	122409	122409	122409	122409	122409	122409	122409
Count,startC1	122250	122250	122250	122250	122250	122250	122251	122250	122250	122250	122250	122250	122250	122250
Count,stopC2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Count,startC2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
f, C1	0.4487	0.4487	0.4487	0.4487	0.4487	0.4487	0.4487	0.4487	0.4487	0.4554	0.4487	0.4487	0.4487	0.4487
f, C2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DE	93	93	93	93	93	93	93	93	93	93	93	94.22	93	93
t	21	21	21	21	21	21	21	21	21	21	21	21	22	21
P	1033	1033	1033	1033	1033	1033	1033	1033	1033	1033	1033	1033	1033	1038
	376.91935	378.53514	376.91935	376.33688	375.7267	374.5636008	379.3049122	376.9193468	376.9193468	371.3739809	376.91935	372.03884	378.20139	375.10374
		1.615798	0	-0.582464	-1.192621	-2.355745917	2.385565486	0	0	-5.545365883	0	-4.8805095	1.2820386	-1.8156038
		2.6108031	0	0.3392641	1.422345	5.549538826	5.690922687	0	0	30.75108278	0	23.819373	1.643623	3.2964171
	8.6673738													
RSD	0.0229953													
		0.0347535	0	0.0045161	0.018933	0.073872337	0.075754359	0	0	0.409341102	0	0.3170701	0.021879	0.04388

Table I10
PC_{10}: tube T136/T137

		Area, C1	Area, C2	a	b	Count,stopC1	Count,startC1	Count,stopC2	Count,startC2	f, C1	f, C2	DE	t	P
		41620	39213	-582.42	882.12	150691	150202	110263	109813	0.4781	0.4673	93	21	1030
		183.128	172.5372	35	2.8	1	1	1	1	0.0021	0.0027	1.22	1	5
Area, C1	41620	41803.128	41620	41620	41620	41620	41620	41620	41620	41620	41620	41620	41620	41620
Area, C2	39213	39213	39385.537	39213	39213	39213	39213	39213	39213	39213	39213	39213	39213	39213
a	-582.42	-582.42	-582.42	-547.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42
b	882.12	882.12	882.12	882.12	884.92	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12
Count,stopC1	150691	150691	150691	150691	150691	150692	150691	150691	150691	150691	150691	150691	150691	150691
Count,startC1	150202	150202	150202	150202	150202	150202	150203	150202	150202	150202	150202	150202	150202	150202
Count,stopC2	110263	110263	110263	110263	110263	110263	110263	110264	110263	110263	110263	110263	110263	110263
Count,startC2	109813	109813	109813	109813	109813	109813	109813	109813	109814	109813	109813	109813	109813	109813
f, C1	0.4781	0.4781	0.4781	0.4781	0.4781	0.4781	0.4781	0.4781	0.4781	0.4802	0.4781	0.4781	0.4781	0.4781
f, C2	0.4673	0.4673	0.4673	0.4673	0.4673	0.4673	0.4673	0.4673	0.4673	0.4673	0.47	0.4673	0.4673	0.4673
DE	93	93	93	93	93	93	93	93	93	93	93	94.22	93	93
t	21	21	21	21	21	21	21	21	21	21	21	21	22	21
P	1030	1030	1030	1030	1030	1030	1030	1030	1030	1030	1030	1030	1030	1035
	220.14338	220.60973	220.63187	219.95515	219.4468	219.9240443	220.3636061	219.893551	220.3943133	219.6733798	219.49612	217.29287	220.89216	219.07988
		0.4663526	0.4884967	-0.188225	-0.696562	-0.219331445	0.220230344	-0.249824762	0.250937568	-0.469995953	-0.6472588	-2.8505086	0.748787	-1.0634946
		0.2174847	0.2386291	0.0354285	0.485198	0.048106283	0.048501404	0.062412412	0.062969663	0.220896196	0.4189439	8.1253992	0.560682	1.1310207
	3.4140405													
RSD	0.0155083													
		0.0186591	0.0204732	0.0030396	0.041628	0.004127285	0.004161185	0.005354681	0.005402491	0.018951819	0.0359433	0.6971197	0.0481038	0.0970361

Table I11
PC_{11}: tube T138/T139

		Area, C1	Area, C2	a	b	Count,stopC1	Count,startC1	Count,stopC2	Count,startC2	f, C1	f, C2	DE	t	P
		33599	30884.5	-582.42	882.12	503731	503152	817673	817024	0.3758	0.4169	93	21	1030
		147.8356	135.8918	35	2.8	1	1	1	1	0.0004	0.0003	1.22	1	5
Area, C1	33599	33746.836	33599	33599	33599	33599	33599	33599	33599	33599	33599	33599	33599	33599
Area, C2	30884.5	30884.5	31020.392	30884.5	30884.5	30884.5	30884.5	30884.5	30884.5	30884.5	30884.5	30884.5	30884.5	30884.5
a	-582.42	-582.42	-582.42	-547.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42
b	882.12	882.12	882.12	882.12	884.92	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12
Count,stopC1	503731	503731	503731	503731	503731	503732	503731	503731	503731	503731	503731	503731	503731	503731
Count,startC1	503152	503152	503152	503152	503152	503152	503153	503152	503152	503152	503152	503152	503152	503152
Count,stopC2	817673	817673	817673	817673	817673	817673	817673	817674	817673	817673	817673	817673	817673	817673
Count,startC2	817024	817024	817024	817024	817024	817024	817024	817024	817025	817024	817024	817024	817024	817024
f, C1	0.3758	0.3758	0.3758	0.3758	0.3758	0.3758	0.3758	0.3758	0.3758	0.3762	0.3758	0.3758	0.3758	0.3758
f, C2	0.4169	0.4169	0.4169	0.4169	0.4169	0.4169	0.4169	0.4169	0.4169	0.4169	0.4172	0.4169	0.4169	0.4169
DE	93	93	93	93	93	93	93	93	93	93	93	94.22	93	93
t	21	21	21	21	21	21	21	21	21	21	21	21	22	21
P	1030	1030	1030	1030	1030	1030	1030	1030	1030	1030	1030	1030	1030	1035
	162.76932	163.17383	163.06834	162.59654	162.2543	162.6080635	162.9311321	162.6627938	162.8761726	162.6698738	162.71953	160.66171	163.32296	161.98299
		0.4045115	0.2990225	-0.172783	-0.515023	-0.161255299	0.161813276	-0.106524993	0.106853774	-0.099445054	-0.04979	-2.1076053	0.5536371	-0.7863252
		0.1636296	0.0894145	0.0298541	0.265249	0.026003271	0.026183536	0.011347574	0.011417729	0.009889319	0.002479	4.442	0.3065141	0.6183073
	2.4499569													
RSD	0.0150517													
		0.0272612	0.0148967	0.0049738	0.044191	0.004332226	0.004362259	0.001890541	0.001902229	0.001647591	0.000413	0.740051	0.0510662	0.1030119

Table I12

PC_{12}: tube S1223/S1224

		Area, C1	Area, C2	a	b	Count,stopC1	Count,startC1	Count,stopC2	Count,startC2	f, C1	f, C2	DE	t	P
		234648.5	242997.5	-582.42	882.12	816896	815912	906662	905776	0.4883	0.5127	100	21	1033
		1032.4534	1069.189	35	2.8	1	1	1	1	0.0035	0.0064	0.8	1	5
Area, C1	234648.5	235680.95	234648.5	234648.5	234648.5	234648.5	234648.5	234648.5	234648.5	234648.5	234648.5	234648.5	234648.5	234648.5
Area, C2	242997.5	242997.5	244066.69	242997.5	242997.5	242997.5	242997.5	242997.5	242997.5	242997.5	242997.5	242997.5	242997.5	242997.5
a	-582.42	-582.42	-582.42	-547.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42	-582.42
b	882.12	882.12	882.12	882.12	884.92	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12	882.12
Count,stopC1	816896	816896	816896	816896	816896	816897	816896	816896	816896	816896	816896	816896	816896	816896
Count,startC1	815912	815912	815912	815912	815912	815912	815913	815912	815912	815912	815912	815912	815912	815912
Count,stopC2	906662	906662	906662	906662	906662	906662	906662	906663	906662	906662	906662	906662	906662	906662
Count,startC2	905776	905776	905776	905776	905776	905776	905776	905776	905777	905776	905776	905776	905776	905776
f, C1	0.4883	0.4883	0.4883	0.4883	0.4883	0.4883	0.4883	0.4883	0.4883	0.4918	0.4883	0.4883	0.4883	0.4883
f, C2	0.5127	0.5127	0.5127	0.5127	0.5127	0.5127	0.5127	0.5127	0.5127	0.5127	0.5191	0.5127	0.5127	0.5127
DE	100	100	100	100	100	100	100	100	100	100	100	100.8	100	100
t	21	21	21	21	21	21	21	21	21	21	21	21	22	21
P	1033	1033	1033	1033	1033	1033	1033	1033	1033	1033	1033	1033	1033	1038
	566.32435	567.51065	567.62381	566.2416	564.5324	566.0499492	566.5993066	565.9905937	566.6588581	564.4008178	562.67445	561.82971	568.25062	563.59639
		1.1863032	1.2994648	-0.082754	-1.791923	-0.274399574	0.274957864	-0.333755094	0.334509343	-1.92353097	-3.6498958	-4.4946377	1.9262733	-2.7279593
		1.4073154	1.6886088	0.0068482	3.210987	0.075295126	0.075601827	0.111392463	0.1118965	3.699971392	13.321739	20.201768	3.7105288	7.4417619
	7.4204929													
RSD	0.0131029													
		0.0255579	0.0306665	0.0001244	0.058314	0.001367418	0.001372988	0.002022974	0.002032128	0.067194366	0.2419332	0.3668799	0.0673861	0.1351482

PC_i (1-12) ALL

#	PC_i	SD	RSD				var		
1	557.29388	19.053356	0.0341891				363.0303884		
2	290.21995	7.7630703	0.0267489				60.26525977		
3	305.27625	3.5062131	0.0114854				12.29353001		
4	303.3582	3.4776252	0.0114638				12.09387721		
5	139.09202	2.7484625	0.01976				7.554046168		
6	239.92801	2.8612092	0.0119253				8.186518244		
7	124.74136	1.6262199	0.0130367				2.644591198		
8	243.88976	3.4166319	0.0140089				11.67337327		
9	376.91935	8.6673738	0.0229953				75.12336925		
10	220.14338	3.4140405	0.0155083				11.65567232		
11	162.76932	2.4499569	0.0150517	PC	SD	U	6.002288687	sum:	var (Measurement uncertainty)
12	566.32435	7.4204929	0.0131029	294.16298	41.86419	83.72838782	55.06371446	625.586629	4.34435159

	SD	RSD
Measurement uncertainty	2.08	0.0070856
D	41.81	0.1421321
PC total	41.86	0.1423163

Component	SD	var	%
Within and between worker, emission from process	41.81	1748.0761	99.93170891
Desorption efficiency	0.770876177	0.594250081	0.033971305
Volume air sampled	0.632471076	0.400019662	0.022867796
Environmental factors during sampling	0.427207141	0.182505941	0.010433259
Analysis	0.133492843	0.017820339	0.00101873
total:		1749.270696	100

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Paper [B]

A REVIEW ON MONITORING EXPOSURE TO SOLID AEROSOLS

[B] A REVIEW ON MONITORING EXPOSURE TO SOLID AEROSOLS

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ABSTRACT

The aim is to review the literature on particle behaviour in air and in the human airways, the sampling theory for aerosols, and sampling equipment, which is currently in use and commercial available.

The concepts and equations are given, which are necessary for understanding the often counter-intuitive behaviour of aerosols in the occupational setting and elsewhere. The mathematical manipulations of the equations have been kept at a minimum; instead transport properties are illustrated by a series of calculations for aerosols consisting of water, minerals, and uranium.

The same concepts and equations are needed to explain and quantify the deposition of particle in the human airways and to design measurement devices. These devices are used for measuring the different aerosol fractions, which will deposit in different parts of the human airways.

A brief description of the human airways is given, which is adequate for the understanding of particles' deposition. The human airways are divided into the extrathoracic, the thoracic, and the alveolar compartment.

The Inhalable, the Thoracic, and the Alveoli Fractions of an aerosol are those fractions, which will penetrate into the extrathoratic, the thoracic, and the alveolar compartments. These fractions are measured using the corresponding Inhalable, Thoracic, and Alveoli (or Respirable) Conventions given in the international standards on sampling of airborne particles: EN481 (1993) (European Commitee for Standardization (CEN), 1993).

The available methods for collecting airborne particles are described and it is discussed to what extend each type of equipment is sampling the aerosol fraction of interest.

No single piece of equipment can measure all types of aerosol, however, some aerosol samplers have proven to be very close to sample in accordance with the convention given in EN481 (1993).

Keywords: Aerosol sampling; Sampling equipment; Deposition of particles

1. Introduction

Humans are exposed to airborne solid particles (solid aerosols) in the ambient environment and at work. Workers are exposed, e.g. in mines during stripping, crushing, grinding, and milling, during transport of the minerals excavated, in workplaces where the minerals are worked-up to the pure elements, compounds or alloys.

Workers working in underground mines are in addition to exposure to airborne dust exposed to a variety of other pollutants, this includes the gases CO, CO_2, NO, NO_2 SO_2, diesel exhaust aerosols, and a variety of aerosol-associated gas-phase hydrocarbons. More than 90% by mass of the diesel exhaust particles have aerodynamic diameters less than 0.1 μm (Willeke and Baron, 1993).

The Mine Safety and Health Administration regulates total dust, quartz, radon daughters, asbestos, and welding fumes (MSHA, 1990).

Airborne particles are encountered as aggregates or agglomerates. A class of solid aerosols of special interest is airborne particles containing toxic trace elements, which may accumulate in the human body.

Solid aerosols are practically never consisting of particles of the same size. In contrast, they usually consist of particles, the sizes of which are widely varying. The size distribution depends on how the particles originally were created and on the history of the particles since their creation.

If particles are inhaled, the size, form, and density of the particles determine where in the human airways they will be deposited. The objective of sampling airborne particles, therefore, is to collect the fractions, which are deposited in different parts of the human airways. The objective of this paper is to review the literature on sampling methods for airborne particles, with special emphasis on particles containing toxic trace elements.

2. Behaviour of airborne particles

The size, form, and density determine the transport properties of particles in air. For understanding human exposure to airborne aerosols and the disposition of particles in the human airways, knowledge is needed about the inhaled particles' transport properties, the speed at which the exposed human is breathing, and on how the human airways are built. The same knowledge is needed to measure exposure correctly.

2.1. Aerosols

Dust is an aerosol consisting of solid particles created by mechanical means, for instance during cutting, crushing, abrasion, grinding, milling done by man, or animals activities, or the nature in general. Dust exists in many sizes. Small dust particles may penetrate as far as the alveoli. Fibers are a subcategory of dust, which also may penetrate into the alveoli even they may be of a considerable length.

Liquid aerosols. A mist is an aerosol of liquid droplets produced by condensation. Droplet sizes are up to a few micrometers (Vincent, 1995). Droplets produced by atomization are generally greater than 5 μm (Cohen and Hering, 1995).

Fumes are aerosols consisting of solid particles produced by condensation of vapours or gaseous combustion products. Usually they are found as aggregates less than one μm consisting of primary particles of a few nanometers. Current interest in atmospheric pollution studies has focused on solid particles in the size range below 2.5 μm, with a finding that they tend to be the fraction formed by gas phase reactions in the atmosphere. Their prevalence can be correlated with specific health effects (Cohen and Hering, 1995). At the workplace fumes are created during welding and soldering.

Smokes and soot. Smoke is an aerosol of solid particles resulting from incomplete combustion. The sizes of smoke particles are usually less than 0.5 μm.

Figure 1.

2.2. Drag forces

2.2.1. Stoke's Law

Stokes law: the drag force acting on a airborne spherical particle is proportional to the particles diameter, proportional to its velocity, and proportional to the viscosity of the fluid, i.e. the air ($\mu_{Air} = 1.81 \times 10^{-5}$ Pa·s):

$$F_{Drag} = -3\ \pi d_p \mu_{Air} v_p \qquad (1)$$

The minus sign indicates that the drag and the velocity are in opposite directions.

To understand flows, the Reynold's number is central. Reynold's number, usually denoted Re is given by:

$$\underline{Re} = \frac{d\, v\, \rho_p}{\mu_{Air}} \tag{2}$$

where d is a characteristic length, μ_{Air} is the air viscosity, and ρ_p is the density of the particle [$kg \cdot m^{-3}$].

2.2.2. Deviations from Stoke's law

Particles, however, fall sometimes slower than calculated using Stoke's law. Stoke's law, therefore, should be modified by three factors correcting for:

1. Slip.
2. Non-Stokesian flow for $\underline{Re} \geq 1$.
3. Non-spherical particle shape.

2.2.2.1. Slip

Air surrounding the particle is not a continuum, but is made up of gas molecules, which are in continuous random motion caused by temperature. For particle with diameters smaller than the mean free path experience the slip phenomenon. The mean free path (mfp) is the mean distance a particle passes before it collides with another particle or an air molecule.

For particles, which are so small that d_p is of the same order of magnitude as the mean free path of the air molecules will experience a slip, which can be corrected for by the Cunningham slip correction factor $C_{Slip}(d)$ (Cunningham, 1910, pp. 357-365):

$$\underline{F_{Drag}} = -\frac{3\pi d_p \mu_{Air} v_p}{C_{Slip}(d)} \tag{3}$$

$$\underline{C_{Slip}(d)} = 1 + \left(\frac{mfp}{d}\right)\left(2.34 + 1.05e^{-\frac{0.39d}{mfp}}\right)$$

Where mfp is the mean free path and d the particle diameter.

Table 1.

Table 1 shows that Cunningham's slip correction is of little significance for particles with diameters above 1 μm. Between 0.1 and 1 μm Cunningham's slip correction raises to almost a factor of three, and below 0.1 μm, it raises dramatically.

The slip phenomenon is illustrated in Figure 2, which shows that small particles experience the air as consisting of atom, molecules, and particles; whereas larger particles experience the air as a continuum.

Figure 2.

2.2.2.2. Non-Stokean flow

The second modification is for non-Stokesian flow. It is of use to discuss this by introducing a drag coefficient: C_{Drag}, which modify the drag equation for spherical particles:

$$F_{Drag} = - \frac{C_{Drag} 3\pi\mu_{Air} d_p v}{C_{Slip}(d)} \quad (5)$$

Table 2.

2.2.2.3. Non-spherical particles

Further, a modification is needed for non-spherical particles:

$$F_{Drag} = - \frac{3\pi\mu_{Air} \phi d_V v C_{Drag}}{C_{Slip}(d)} \quad (6)$$

where d_V is the equivalent volume particle diameter and ϕ is the shape factor.

Table 3.

Besides the drag force, which describes the air resistance to the particles motion, other forces exist: Forces due to gravity, moving air, electrostatic forces, and concentration and thermal gradients. The set of equations needed to describe particle motions in general becomes quite complicated. In this paper, only single examples will be given and their relative influence on particles' movement will be calculated.

2.3. External forces

2.3.1. Force of gravity

Particles in a gravity field are influenced by the force of gravity, the drag force, and a force due to buoyance. The later is according to the law of Archimedes (Archimedes, ca. 287 – ca. 212 BC), which says that a body in a fluid is acted on by a force equal to the weight of the fluid it has displaced. Newton second law:

$$\frac{mdv_p}{dt} = m \times g = F_{Buoyance} + \frac{3\pi\mu_{Air} d_p v_p}{C_{Slip}(d)} \qquad (7)$$

$F_{Buoyance}$ is the force due to buoyance, which may be neglected, as the density of air is 1.29 $kg \cdot m^{-3}$ at STP, whereas density of, e.g. water is 1000 $kg \cdot m^{-3}$. Rearranging gives:

$$\frac{dv_p}{dt} + \frac{v_p}{\tau} - g = 0 \qquad (8)$$

where $\tau = C_{Slip}(d)\, d_p^2\, \rho_p / 18\, \mu_{Air}$ [s]. τ is called the particle relaxation time, which is the time it takes for the particle to come into dynamic equilibrium with the forced acting upon it, i.e., in the case of a falling particle, the time it take to reach its terminal or sedimentation speed. d_p is the particle diameter [m] and ρ_p is the particle density [$kg \cdot m^{-3}$]

Figure 3.

Table 4.

It is of note that the relaxation times are very short. The equation may be solved, giving:

$$\underline{v_p} = \underline{g\,\tau}\left[1 - e^{-\frac{t}{\tau}}\right] \tag{9}$$

For $\underline{t} >> \underline{\tau}$ ($\underline{t} > 3\underline{\tau}$ is suggested by Hinds. (Hinds, 1999)), the terminal falling speed or sedimentation speed is:

$$v_s = g\,\tau \tag{10}$$

Substitution for $\underline{\tau}$ gives:

$$v_s = \frac{\rho_p\, g\, d_p^2}{\left[\frac{18\,\mu_{Air}\,\phi}{C_{Slip}(d_p)}\right]} \tag{11}$$

Sedimentation rates for spherical particles (for which $\underline{\phi} = 1.00$) are calculated in Table 5:

Table 5.

The density of uranium is about 19 times the density of water. This difference in density causes a particle of uranium to have a sedimentation velocity 19 times higher than a water droplet of the same form and diameter. The sedimentation velocity is proportional to density: $\underline{v_s = k_1\,\rho}$. Particle diameter has a more profound influence: $\underline{v_s = k_2\,d^2}$. The sedimentation velocity of a particle having a diameter of 100 μm is more then 4000000 times that of a particle of the same material and shape with a 0.01 μm diameter.

2.3.2.Particles in moving air (or moving particle in stagnant air)

Movement of particles influenced by no external forces in the direction of their movement can be described in two scenarios: 1. The initial velocity of the particle is zero and the air is moving. 2. The initial velocity is finite, but the air is stagnant. The two scenarios are equivalent; it depends on the definition of the coordinate system (G. Galilei, 1564 - 1642).

The stop distance is the distance a particle, which has a finite velocity, travels before it comes to rest relative to the air, i.e. becomes in dynamic equilibrium with the air. If a particle with zero velocity in the air's flow direction is injected into airflow it will at first lag behind the air. The drag force extended by the flowing air will gradually increase the velocity of the particle until it reaches the same speed as the air. The particle has become airborne.

$$m\left(\frac{dv_x}{dt}\right) = -\frac{3\pi\mu\, d_p v_x}{C_{Slip}(d)} \tag{12}$$

which solved gives:

$$v_x = v_{x0}\, e^{-\frac{t}{\tau}} \tag{13}$$

where v_{x0} is the speed relative to the air at $t = 0$; and with further manipulation:

$$s = v_{x0}\,\tau \tag{14}$$

where s is the stop distance: the distance travelled by the particle before it comes to rest – or, changing viewpoint, the distance travelled before it achieves the same velocity as the moving air.

Table 6.

Initial velocity of 3.27 $m \cdot s^{-1}$ is the linear velocity of air in the human throat (see Table 6) Considering spherical particles of uranium injected into stagnant air having an initial velocity

of 110 $km \cdot h^{-1}$: A 100 μm particle will stop after approximately 18 m, whereas a 0.01 μm particle will stop after 4.0×10^{-6} m or 4.0 μm.

2.3.3. Particles in electric fields

Only recently, electrical properties have been given attention in aerosol science. A growing number of investigations have shown that the electrical properties of aerosols have a substantial practical relevance, e.g. on deposition in the lungs, when sampling airborne aerosols, and when the air is cleaned by filtration.

Johnston et al. found, irrespective of the type of aerosol and how they were generated that each particle was charged either net positive or net negative and that the distribution of charges were almost symmetrically between positive and negative (Johnston et al., 1985, pp. 271-284). The aerosols as a whole, therefore, were close to neutral. They also found that the median charge per particle (q_m) could be expressed as

$$\left|\frac{q_m}{e}\right| = A\, d^n \qquad (15)$$

The electron charge, $e = 1.6 \times 10^{-19}$ C (Coulombs). A and n are constants, the sizes of which depend on the material considered and the process during which the particles are created (See Table 7) below.

The charge per particle of fibres, e.g. asbestos is relative independent of the fibre diameter, but approximately proportional to its length:

$$\left|\frac{q_m}{e}\right| = \sigma L \qquad (16)$$

where σ is the charge per unit length of the fibre. σ is a constant of proportion, which depends on the material considered and the process during which the particles are created (See Table 7) below. L is the length of the fibre.

Table 7.

Electrostatic force is of relevance for deposition in the alveoli and when sampling particles carrying electrical charges:

$$F_C = \frac{q^2 \, x \, R}{4\pi\varepsilon_0 (R^2 - x^2)^2} \qquad (17)$$

ε_o is the permittivity of vacuum = 8.85×10^{-12} A s V^{-1} m^{-1}. R is the alveoli radius and x is the distance of the particle from the centre of the alveoli sac. It is of note that the electrostastic force rises sharply, when the particle approaches the alveoli wall, because $(R^2 - x^2)^2$ approaches zero.

2.3.4. Thermal gradients

Airborne particles will, if they experience a thermal gradient, receive more momentum from the colliding air molecule from the hot than from the cold region, because the warmer molecules have higher velocities. Therefore, a net force is acting in the direction from the hot to the cool region.

For particles with diameters close to mean free path in air (= 6.6×10^{-8} m at STP) the thermophoric velocity is:

$$v_T = -k_1 \Delta T \qquad (18)$$

where k_1 is a constant, which does depend on the local temperature (T) but not on particles size or composition, when the particle is small. ΔT is the temperature gradient and the minus sign indicates the direction of the thermophoretic motions towards the cold region. The thermophoretic drift has been estimated to be of the order of 2×10^{-6} $m\cdot s^{-1}$ per K (Vincent, 1995). Compare with Table V. For a thermal gradient of 1 $K\cdot cm^{-1}$ the thermophoretic velocity of a 0.01-μm particle is 42 times the terminal sedimentation velocity. For a 0.1-μm particle it is 2.3 times and for a 1-μm it is 0.04 times. Compared with deposition due to Brownian diffusion, deposition due to thermal gradient of a 1 $K\cdot cm^{-1}$ is 0.1 times the deposition due to diffusion. For a 0.1-μm particle it is 0.7 times and for a 1-μm particle it is 2.2 times.

For larger particles the size and composition of the particle cannot be ignored, e.g. the temperature gradient within the particle must be taken into consideration.

Not mentioned in this going through external forces, which influence particles are magnetic and photophoretic forces.

2.3.5. Brownian diffusion

The smooth motion of small airborne particles have a random movement superimposed the motion due to external forces described above. The random motion is due to collisions with other particles and with air molecules, which themselves are in thermal motion. The phenomenon is called Brownian motion after R. Brown (1827). When a concentration gradient exists, the particles will experience more collisions if their random walk is up the concentration gradient than when it is down the concentration gradient, resulting in a net flux of particles down the gradient, the more the steeper the gradient. Fick's first law describes this phenomenon:

$$\frac{dN}{dt} = -D\,A\left(\frac{dC}{dx}\right) \tag{19}$$

where N is number of molecules (or mass), which travels in the x direction per second through the area A caused by the number or mass concentration gradient dC. The coefficient D [$m^2 \cdot s^{-1}$] is called the diffusion coefficient. It can be calculated from kinetic theory:

$$D = \frac{kT}{\left[\frac{3\pi\mu_{Air} d_p}{C_{Slip}(d_p)}\right]} \tag{20}$$

k is the Boltzmann's constant (= 1.38×10^{-23} $J \cdot K^{-1}$), T is the absolute temperature [K], μ_{Air} is the viscosity of air (=1.81×10^{-5} Pa·s), and d_p is the particle diameter [m]. $C_{Slip}(d_p)$ is the Cunningham slip correction factor for the particle. It is of note that the numerator represent the thermal energy of the gas molecules transferred to the particles and the denominator in the squared parenthesis represent the loss of particle kinetic energy due to viscous effects. The diffusion coefficient, therefore, embodies the continual interchange of thermal energy between the gas molecules and particles and vice versa (Vincent, 1995).

Table 8.

For comparison, the diffusion coefficient of air molecules is $1.99\times10^{-5}m^2\cdot s^{-1}$. Thus the air molecules in average will diffuse 365 times faster than a particle with a diameter of 0.01 μm, 727000 times faster than a particle with a diameter of 1 μm, and 83786000 times faster than a particle with a diameter of 100 μm.

2.3.6. Turbulent Flow

In laminar flow of air, the air layers slide smoothly over one another. But if the forces involved are much larger than the viscous forces, i.e. Reynolds number (Re) is large enough, then the flow will be instable resulting in a random-fluctuating motion superimposed on the mean flow (Vincent, 1995), which cause a apparent increase in viscosity.

Turbulence is an extremely complex phenomenon, which cannot be treated in details in a single paper. However one should notice that the diffusivity of turbulent air movement is of the order of the order 10^{-3} $m^2\cdot s^{-1}$ (Vincent, 1995), whereas diffusion of carbon dioxide due to Brownian motions has a diffusion coefficient of 1.39×10^{-5} $m^2\cdot s^{-1}$, which is 100 times lower. Transport of airborne particles in air, therefore, is not primarily due to Brownian diffusion, but due to turbulent air eddies, caused by draft and air warmed up by machines and humans.

2.4. Agglomeration

Small particles agglomerate when colliding with one another, resulting in a decrease in the number concentration and the surface concentration. The mass and volume of the single particle increases, whereas the total mass and volume of the aerosol obviously stay constant.

The deviation of equations in the general case is rather complicated. For the simple case of monodisperse spherical particles the change in number concentration:

$$\frac{dn}{dt} = -4\,\pi d_p D_p n^2 = -K n^2 \tag{21}$$

where $\underline{K}$ is called the agglomeration coefficients, which is equal to $4\pi\underline{d_p}\underline{D_p}$ [$m^3 \cdot s^{-1}$] an expression, which needs correction (Hinds, 1999).

Table 9.

$$n(t) = \frac{n_0}{1 + n_0 K t} \tag{22}$$

where $\underline{n_0}$ is the number concentration at $\underline{t} = 0$.

$$d(t) = d_0 \sqrt[3]{1 + n_0 K t} \tag{23}$$

thus, when the diameter of the particles is doubled then the number concentration is decrease with a factor of eight. This simple equation is valid only for monodisperse pherical particle, which agglomerate into monodisperse spherical particle without pores. Porous agglomerates will grow fasters than predicted by the equation.

Table 10.

Table 10 defines concentration regions where agglomeration can be neglected. Agglomeration will not be substantial if the concentration is less than 10^{12} ptc m^{-3}, when sampling for 15 minutes. Indoors, Hinds suggested to neglect agglomeration when the number concentration is below 10^{12} pct m^{-3} (Hinds, 1999).

For calculation on polydisperse spherical particle aerosols having a lognormal size distribution see (Hinds, 1999).

Table 11.

2.5. Adhesion of particles to surfaces

Adhesive forces can be measured as the force required separating a particle from a surface. For hard materials and clean surfaces an expression for the adhesive force is given, based on direct measurements:

$$F_{Adhesive} \approx 0.063\, d_p [1 + 0.009(\%RH)] \qquad (24)$$

Where %RH is the relative humidity expressed in per cent (Hinds, 1999).

Adhesive forces are proportional to d_p, but removal forces (e.g. vibration) are proportional to d_p^3 whereas removal forces for air current are proportional to d_p^2. That is, small particles are more difficult to remove than larger particles. Table 11 shows the adhesive force for particles with diameters less than 100 μm (Hinds, 1999). The adhesive forces are larger than forces due to gravity and air currents. The more, the smaller the particles.

2.6. Deposition of particles on surfaces

Solid particles adhere when they collide with surfaces. The aerosol concentration at the surface, therefore, is zero and consequently a concentration gradient exists, which maintain a flux of particles from the bulk air to the surface. The particle number concentration n(x,t) in distance x at time t must satisfy Fick's second law:

$$\frac{dn}{dt} = D\frac{d^2n}{dx^2} \tag{25}$$

and Fick's first law

$$\frac{d\left(\frac{N}{A}\right)}{dt} = -D\frac{dn}{dx} \tag{26}$$

Combining these equations gives the cumulative deposition per unit area due to Brownian diffusion:

$$\frac{N(t)}{A} = 2n_0\sqrt{\left(\frac{Dt}{\pi}\right)} \tag{27}$$

The equation applies only to a large aerosol volume, where n_0 is constant, i.e. it gives the upper limit of the deposition rate per square meter.

Table 12.

For large particles, settling is the dominating mechanism of deposition of particles. For smaller particles the dominating mechanism is diffusion.

Figur 4.

3. The human respiratory tract

The primary objective of the human respiratory tract is to supply the body with oxygen and to excrete carbon dioxide and other gases. The air is inhaled through either the nose or the mouth. In the nose, the air is warmed and humidified before it is entering the lungs. The surface of the nose is ciliated, so foreign particles are transported in the mucous layer. In the anterior parts of the nose particles are cilated forwards (half-life about 24 hours) in the back of the nose particles are ciliated backward towards the throat (half-life about 10 minutes) where they can be swallowed (Schneider, 1996).

A simple model of the human airways is shown in Figure 4. In Weibel's model the lungs consist of bronchioles, which for each generation branches into two (Weibel, 1963). In total 24 generations. The airway diameter is reduced following an exponential function:

$$d_z = d_0 \, 2^{-z/3} \qquad (28)$$

where d_z and d_0 are the diameters in generation z and 0 respectively. This relation is known to reflect and optimal design for mass flow of air with minimal energy loss (Annals of the ICRP, 1993). Table 13 shows the size of the airways and the flow conditions:

Table 13.

Above the respiratory bronchial region the surfaces are covered with cilia and mucous layer, which transport foreign particles upwards towards the larynx for eventually being eliminated through the gastrointestinal tract. The half-life is about 2 hours (Schneider, 1996).

The tidal volume is about 0.5 dm^3 at rest and the reserve air volume is 2-3 dm^3. The maximal volume of air inhaled is about 2 dm^3. In the alveoli the mixing does not take place by convection but by diffusion. As there are no cilia in the alveolar region, the alveoli are not cleared by this mechanism. Instead clearance is performed by macrophages present on the surface of the alveoli.

Typically the volumetric flow rate is 7 $dm^3 \cdot min^{-1}$, which increased to above 20 $dm^3 \cdot min^{-1}$ during moderate to hard work. The frequency of inspiration is about 12 times per minute (Schneider, 1996). As a rough conservative estimate, a person working inhales and exhales 10 m^3 per 8 hour working time.

4. Deposition of particles in the human airways

4.1. Aerodynamic Diameter

Particles suspended in air move under gravimetrical, electrostatical, and thermophoric forces. The movement depend on the particle's size, form, density, etc. All these variables can be summarized in the concept of the aerodynamic diameter.

A particle's aerodynamic diameter is the diameter of a spherical droplet with a density of 10^3 kg·m^{-3} (density of water at 4 °C), with the same terminal velocity in calm air as the particle considered (European Commitee for Standardization (CEN), 1993).

$$d_{Ae} = d_V \sqrt{\frac{\rho\, C_{Slip}(d)\, C_D^*\, \mathrm{Re}_p^*}{\rho^*\, C_{Slip}(d)^*\, C_D\, \mathrm{Re}_p\, \phi}} \qquad (29)$$

where dAe is the aerodynamic diameter, d_V is the volumetric based diameter, ρ is the particle diameter, $C_{Slip}(d)^*$ is the Cunningham slip factor. C_D^* is the drag factor, Re_p^* is the Reynolds number, and ρ^* is the density for the particle respectively for the particle. $C_{Slip}(d)$, C_D, and Re_p are the corresponding values for the equivalent aerodynamic particle. ϕ is the form facto

Figure 5.

For thin fibres, e.g. asbestos, (Cox, 1970, pp. 791-798) derived the following aerodynamic diameter when the fibre falls with its axis perpendicular to the direction of motion:

$$\left(\frac{d_{Ae}}{d}\right)^2 \left(\frac{\rho^*}{\rho}\right) = \frac{9}{8}\left(\ln\left(\frac{2L}{d}\right) + 0.193\right) \qquad (30)$$

and for falls with the axis parallel to the direction of movement:

$$\left(\frac{d_{Ae}}{d}\right)^2 \left(\frac{\rho^*}{\rho}\right) = \frac{9}{4}\left(\ln\left(\frac{2L}{d}\right) + 0.807\right) \qquad (31)$$

where L is the length and d the diameter of the particle, respectively. Experiments on amosite asbestos suggest that these fibres fall with their axis close to horizontal (Stöber, 1971, pp. 453-456).

4.2. Aerosol fractions

Depending of the particles' aerodynamic diameters, an aerosol can be divided into fractions after their behaviour in the human airways: 1. **Inhalable** (or inspirable) **Fraction**: the fraction of total airborne particles, which is inhaled through the nose. It depends on speed and direction of the air movement, breathing rate, and other factors. 2. **Thoracic Fraction**: the fraction of inhaled particles, which can penetrate beyond the larynx. 3. **Alveolar Fraction**: the fraction of inhaled particles, which can penetrate to the unciliated airways. (European Commitee for Standardization (CEN), 1993) calls this fraction the respirable fraction meaning particles, which can penetrate to the alveolar, but also can be exhaled again.

5. Conventions for sampling instruments

It is of special importance for assessing risk of adverse health effect in humans exposed to aerosols to measure the fractions, which are deposited in the upper airways, the thoracic region, and in the alveoli. Because all measuring instruments are size selective to some extent, it is often impossible to measure the total airborne particle concentration. The Inhalable Convention is the target specification for sampling instruments, when measuring the Inhalable Fraction. The Thoracic Convention is the target specification for sampling instruments, when measuring the Thoracic Fraction, and the Alveolar (Respirable) Convention is the target specification for sampling instruments, when measuring the Alveolar Fraction.

Inhalable Convention is given by

$$E_{Inhalable} = 50\left(1 + e^{-0.06\, d_{Ae}}\right) \qquad (32)$$

d_{Ae} is in µm. (EN 431, 1993)

Thoracic Convention ($E_{Thoracic}$) is given by the cumulative lognormal distribution with a median of 11.64 [µm] and a geometric standard deviation of 1.5. (European Commitee for Standardization (CEN), 1993)

Alveolar (Respirable) Convention ($E_{Alveolar}$) is given by the cumulative lognormal distribution with a median of 4.25 [μm] and a geometric standard deviation of 1.5. (European Commitee for Standardization (CEN), 1993)

Figure 6.

5.1. Particles deposited in the human airways

Particles deposit in the human airways by a complex action of the five deposition mechanisms:

1. Interception
2. Inertial impaction
3. Diffusion
4. Gravitational settling
5. Electrostatic attraction

The extrathoracic deposition refers to particles, which are deposited in the upper airways. The deposition during mouth breathing is quite different from deposition when the person is breathing through nose, but in both cases mainly due to impaction and to a lesser degree due to gravity. Electrostatic deposition has been shown to be minute (Fry, 1970, pp. 135-146). The particles deposited in the upper airways compartment become equal to:

$$E_{Inhalable} - E_{Thoracic}.$$

Because of the high air velocity in the thoracic compartment, particles are deposited due to impaction. (Yu, 1985, pp. 219-227) found that electrostatic deposition is small. The deposition becomes equal to:

$$E_{Thoracic} - E_{Alveolar}.$$

The low air velocities in the alveoli make deposition by impaction almost not existing. Gravitational settling, electrostatic forces and diffusion deposit the particles, which enter the alveolar region.

Table 5 shows that the terminal sedimentation rate is very low for small particles, but the distance they must travel in order to reach the lung surface is only a fraction of the diameter of the alveolar sacs, which is of the order of 300 μm. The largest of the particles deposit, therefore, mainly due to gravimetrical settling, because, of the particles capable to penetrate to the alveolar region, they have the smallest diffusion coefficients.

The smallest particles have the highest diffusion coefficients, but the smallest sedimentation rates. It therefore follows that efficiency of deposition as function of geometric diameter goes through a minimum considering particles of the same density.

Table 14 shows deposition of particles in the different compartments of the airways as function of aerodynamic diameter. Particles above 10 μm do not penetrate into the alveoli, because they are deposited in the upper airways.

In the alveolar region a substantial contribution to deposition comes from electrostatic deposition. Especially thin ($d \approx 1$ μm), long fibre may have a very small aerodynamic diameter. Such fibres can therefore penetrate into the alveoli. Despite their small aerodynamic diameter, they are geometrically large and can therefore carry a large electrical charge, which make electrostatic deposition likely.

Table 14.

Some of the particles penetrating into the alveoli region remain airborne and are therefore exhaled. The efficiency of exhalation, E_{exh}, is given by:

$$E_{Exh} = 1 - E_{Totdep}$$

The amount of particles exhaled has been calculated as the amount of the fraction of particles inhaled, which has not been deposited in the exthoracic, the thoracic, and the alveoli compartment (Vincent, 1995).

The particles deposited in the alveolar compartment becomes equal to:

$$E_{Alveolar} - E_{Exhaled}.$$

Particles must deposit to have a biological effect. The measuring conventions, therefore, underestimate the biological effect of a given amount of deposited particles, which penetrate to the alveolar compartment, because what is measured is the amount reaching the compartment ($E_{Alveolar}$), not the amount deposited ($E_{Alveolar} - E_{Exhaled}$). If the mass of particles inhaled is of concern, the mass of the exhaled particle may be disregarded for two reasons: the measured result is conservative and the mass of the minor particles which reach the alveoli is only small, compared with the mass of the total aerosol inhaled.

6. Distributions of airborne particles

The objective is to investigate which measures of exposure are relevant for different types of aerosols:

Particle Number Distribution is of concern when risk is related to number of particles inhaled. This is for instance the case when aggregates of infectious microorganisms are measured. (Peters et al., 1997, pp. 1376-1383) found that respiratory effects were associated with the number of ultrafine particles. When analysis is done by microscope, number distribution is an obvious choice for characterising the exposure.

Volume Distributions or particle diameter distributions is often measured, when samples are analysed by mean of microscopes.

Surface Distribution is of concern, when the toxic or corroding substance is adsorbed on the surface of dust particles. Exposure to surface area per day is the dose, which predicts pulmonary disease (Donaldson et al., 2001, pp. 211-216).

Mass Distribution is of concern, when all particles have the same percentage (by weight) of the element or compounds considered and risk is related to the number of moles of toxic elements or compounds.

Distribution of Trace Element is of concern when the percentage of the toxic elements or compounds considered depends on the size of the particles.

7. Visibility

The wavelength of light range from approximately 0.39 μm (blue) to 0.78 μm (red) that is of the same order of magnitudes as some types of aerosols, see Figure 1. The light absorbs into the particles or is reflected (scattered) from the particles' surfaces. The absorption and scattering together is called the extinction. What happens depends on the diameter of the particles, the concentration, the wavelength of the light, etc. The sky looks blue because the blue wavelengths of the white sunlight are reflected more than the red wavelengths in the air

molecules and the aerosols of the atmosphere. The red colour of the sunset is caused by the same phenomenon. At sundown, the light travels a longer distance through the atmosphere and almost all blue wavelengths are absorbed or scattered, while the red wavelength are passing through. The extinction is largest for particles, the diameters of which are close to the wavelength of the light. For the same mass concentration, tobacco smoke looks ten times denser than an aerosol of wood dust with a mean particle diameter of about 6 μm (Schneider, 1996).

Without aid, it is possible for humans to see particles down to approximately 50 μm. Smaller particles can only be seen if they are reflecting light and particles with diameters below 10 μm, can only be perceived as "fog". In the literature it has been demonstrated that it is not possible to graduate, not to speak of to quantify, air concentration by observation alone (Woitowitz et al., 1970, pp. 419-422).

If it is important to know the air concentration of particles in a given area, the concentration must be measured with one or more suitable method, some of which are described below.

8. Methods for measuring exposure to airborne particles

The first objective is to investigate, which sampling devises are available for collecting different fractions of solid aerosols, when sampling particulate matter.

The second objective is to give the reader a background knowledge from which to choose between alternative methods for sampling solid aerosols, based on knowledge of the aerosols' distributions, using the theoretical information given above.

8.1. Air movers

A series of consideration must be taken, before selecting and/or buying air movers. The quantification limit of the analytical procedure and the sampling time determine, together with the expected air concentrations relative to the concentration levels of concern, the minimum demand to the capacity of the air moving equipment.

The maximum demand depends on the capacity of the collection medium. If filters are overloaded they clocks and resistance is building up slowing down the sampling rate. Sampling rate determines what size of particulate matters will be removed most efficiently

and therefore, distorting the measurement as far as concern the determination of the exposure and therefore the health risk.

Sometimes recommended sampling rates and total sampling times can be found in the literature. For instance Coal Mine Safety and Health Administration (1992) prescribes a flow rate of 2 $dm^3 \cdot min^{-1}$. US Environmental Protection Agency (1992) prescribes 1.13 $m^3\ min^{-1}$ for PM_{10} sampling of ambient particulate matter.

However, such data are much easier and cheaper provided via the Internet. A search on www.google.com using the key words: sample time sample rate and minerals gave 9080 hits in 2.79 seconds.

Before selecting and buying equipment also more practical problems must be considered e.g. difficulties involved in calibration and maintenance, the power supply available, i.e. availability of line current, generators, batteries, hand powered generators. Further, when sampling in flammable and/or explosive atmospheres equipment must be secure to use in such places. Measuring corrosive atmospheres or in very cold or very hot places, may require equipment consisting of special materials.

8.2. Collection devises

Devises for collecting particulate matter must do that isokinetic, i.e. sampling must be done in such a way that the size distribution of the particulate matter sampled is the same as in the sampled air. Sampling for instance is anisokinetic when it is performed in a flowing stream without aligning the collecting probe with the streamlines. When sampling from still air, a bias result when sampling at low rate and the inlet tube is facing upwards (positive bias) or downwards (negative bias).

For continuous sampling of particulate matter, several physical factors including gravity, interception, impaction, electrophoresis, thermophoresis, and diffusion are employed. Collector of aerosols can be divided into the following categories, which is treated below:

8.2.1. Settling chambers

8.2.2. Centrifugal devises (e.g. cyclones)

8.2.3. Impingers and impactors

8.2.4. Bubblers

8.2.5. Filters

8.2.6. Electrostatic precipitators

8.2.7. Thermophoretic precipitators

8.2.8. Diffusion batteries

8.2.9. Passive personal dust sampler

8.2.10. Direct reading instruments

Non-size selective sampling

8.2.1. Settling chambers

Elutriators, i.e. chambers in which the air is calm undistorted settling can take place due to gravitation. Sampling rates depend strongly on particle diameter and particle density (see Table 5 and 7).

Size selective sampling

8.2.2. Centrifugal devises

The range for human variation for lung retention is probably as great as for most physiological characteristics and changes in breathing rate and volume per breath. It profoundly affects the size retention characteristics of the respiratory system (Cohen and Hering, 1995). Nevertheless, sampling devises have been invented, which tries to simulate a standardised human lung particle size rejection curve. For the outdoor environment, size selective samplers have been developed with cut points of 2.5 and 10 μm in aerodynamic diameter. The rationale is that the smaller particles originate from gas phase reaction in the atmosphere that produce acid aerosols whereas the largest ones tend to come from stack emissions of solid particles plus windblown mineral particles (Cohen and Hering, 1995). Table 4 and 6 show that particles with a small diameter have very small relaxation times, and short stop distances. If such particles pass a cyclone they will be separated from the larger particles. The alveolar fraction, e.g., can be sampled separately.

Further, personal sample equipment exists, which sample all three fractions simultaneously. See e.g. http://www.tsi.com/hsi/homepage/respicon/respspec.htm

8.2.3. Impingers and impactors

Impingers and impactors use the particle's momentum for collecting it. Impingers consist of glass nozzle submerged in a suitable liquid for collecting. The linear speed at the nozzle ranges from 60 – 113 $m \cdot s^{-1}$ (Cohen and Hering, 1995). Cascade impactors collect on a dry or reased slide. They contain a number of stages which progressive separation of smaller and smaller particles as the aerosol travels through the unit.

8.2.4. Bubblers

The midget impinger is the most widely used of this type of instruments. When used as a bubbler in general, it is filled with 10-20 ml absorbing solution. The flow rate 1.0 $dm^3 \cdot min^{-1}$. A source of suction (for instance a personal pump) is connected to the outlet tube. The impinger is either hand-held or attached to the clothing of the person monitored (Cohen and Hering, 1995).

8.2.5. Filters

Filters remove particles from the air by a series of mechanisms. Interception of the particle by the filter material is important when the ratio of the particle size to the pore size is large. Inertial collection occurs when the airflow suddenly changes direction whereby the particles, which have more inertia, and therefore tends to keep the direction hit the surface of the filter. High air velocity and dense filter packing favour this mechanism.

Diffusion is important for small particles. Diffusion is favoured by high particle concentration and low air velocity. The efficiency increases with decreasing particles. For particles with a diameter below 0.01 μm, however, particle rebound from the surface (Wang and Kaspar, 1991, pp. 291).

Electrical force might contribute substantially to collection efficiency. Data needed to predict the effect of electrostatic charges on collection efficiency, however, are seldom available (Cohen and Hering, 1995).

Gravitational forces can be neglected except when wind air velocity is extremely low, for instance below 0.05 $m \cdot s^{-1}$ (Cohen and Hering, 1995).

It is not always possible to have a high collection efficiency for all particle sizes, because that would restrict the number of possible filters unacceptable for other reasons, e.g. cost, fragility, etc. It is of note that if the relevant measure of exposure is mass concentration, then it is important effectively to collect the larger particles as they contribute most to the total mass collected, whereas sub-micrometer particles only contribute very little. When number of particle, which will reach the alveoli compartment, is the relevant measure of exposure, large particles might be ignored.

Filters made by fibres of cellulose, glass, quarts, asbestos, and plastic of different compositions are commercial available. Other filters are made from sintered granular bead of glass, aluminium oxide, silver granules and (gel-type) membrane filters. Nucleopore filters are made by exposing a polycarbonate film for a flux of neutrons followed by etching the neutron tracks chemically.

Application of a low-cost, dual-fraction dust sampler has recently been described (Kenny et al., 2001, pp. 35-42). The dust sampler measures both inhalable and respirable dust concentrations in a single sample, thus it saves both time and money.

The best source of information about the properties and use of filters can be obtained from the suppliers of filters. Suppliers can be found on the Internet.

Recently, (Görner et al., 2001, pp. 43-54) carried out a study in which fifteen aerosol samplers were compared systematically. Of six inhalable aerosol samplers tested only one (RespiCon) was able to match the Inhalable Convention fairly, using monodisperse solid particles with aerodynamic diameters ranging from 5 to 68 μm. The other five samplers depended on wind speed, when wind speeds are above 0.5 $m \cdot s^{-1}$, wind direction, and particle size (Li et al., 2000, pp. 506-516).

Table 15.

8.2.6. Electrostatic precipitators

The principle of electrostatic precipitators is to charge the particles and subsequently precipitate them in an electric field. In contrast to filter samplers, mass load does not affect sampling rate due to clogging.

Particles with a diameter larger than approximately 0.5 μm have a too large inertia to be precipitated in this type of samplers. When sampling with electrostatic precipitators, adhesion is of primary importance because the electric force does not in general hold the dust onto the surface (Penney, 1962, pp. 301).

Maximum collection efficiency in a precipitator sampler is obtained applying high voltage. Visual examination can provide a useful indication of the collection efficiency. If sampling efficiency approaches 100%, there should be no significant deposit for the last few centimetres of the collector.

8.2.7. Thermophoretic precipitators

The principle of thermophoretic precipitators is, that particles are precipitated when passing through a narrow channel, which has a temperature gradient of 1000 – 10000 K cm^{-1} perpendicular to direction of flow. This method is useful for particles with diameters between approximately 0.01 and 0.5 μm, because the thermophoretic velocity does not decrease with particle size. Sampling of particles with diameter larger than approximately 5 μm is connected

with upstream difficulties due to gravitational and inertial effects. Flow rate is usually between 10 and 1000 $cm^3 \cdot minutes^{-1}$.

Thermal precipitators are not suitable for collecting volatile aerosol particles. Generally, thermal precipitators are useful aerosol devices, especially for sub-micron particles.

The advantages of thermophoretic samplers are that no alignment take place, which could distorts particle size determination, when analysing using microscopes and that precipitation is so gentle that agglomerates seldom breaks up.

8.2.8. Diffusion batteries

Particles are separated according to their diffusion coefficients by measuring the concentration of particles entering and leaving a tube or other similar conduit. Diffusion batteries are used for measuring the particle size distribution of sub micrometer particles with diameters of approximately 0.002 to 0.2 μm (Hinds, 1999).

Two types of diffusion batteries exist: 1) Single-stage diffusion batteries (based on rectangular channels or parallel circular plates) and 2) several stage diffusion batteries (cylindrical-tube and screen-type). Single-stage diffusion batteries can be used for measuring diffusion coefficients of mono-disperse aerosols at one flow rate.

In diffusion batteries a condensation nucleus counter in a sampling train is often used for detection of aerosol penetration.

8.2.9. Passive personal dust sampler

In this passive dust monitor are particles deposited by gravitation and Brownian and turbulent diffusion onto three transparent sticky foils facing upwards, forwards and downwards. After sampling, the foils are analysed by light extinction measurements or examined in a microscope (Vinzents, 1996, pp. 261-280). Size and number distribution can be measured and the unbiased volume weighed diameter distribution can be calculated from the forward foil.

Airborne particles of all sizes are collected by this method. The monitor is for personal sampling and it is fixed in the breathing zone by use of a light harness. It is easily handled and the foils can be sent by mail and is thus suitable for self-administered studies.

8.2.10. Direct reading instruments

Direct-reading field instruments for aerosols measurements combine sampling and analysis.

8.2.10.1. Piezoelectric sensor

Electrostatic precipitation particles are deposited on a piezoelectric sensor and particle mass is measured (TSI, 2001). Rate of change of the resonant frequency of the sensor is directly proportional with the mass of material deposited on it. Short period slopes (24-120 seconds) can be analysed to measure concentration fluctuations. The instrument is capable of measuring particle mass concentrations as low as a fraction of a few mg m^{-3} at a sampling rate of 1.0 $dm^3 \cdot min^{-1}$ over a period of 2 minutes (Cohen and Hering, 1995).

8.2.10.2. Beta-ray measurement

In this type of instrument the attenuation is directly related to the mass of collected particles in the beam. In the instrument, a ^{14}C beta source is used in combination with a solid-state, silicon surface-barrier detector to measure the attenuated beta radiation.

8.2.10.3. Light scattering

Two different types of instruments have been reported in Europe. The Safety in Mines Light Scattering Instrument (SIMSLIN) is a horizontal elutriator system (British), in which the aerosol is passed through the plates of a horizontal elutriator designed to have penetration characteristics matching the British Medical Research Council (BMRC) respirable aerosol curve. In the instrument the particles deposit on a filter. A time-weighted average of the respirable aerosol mass concentration can be obtained by weighing the filter at the end of a sampling shift. The aerodynamically selected aerosols enter an optical zone in which scattered infrared light (a diode laser) is collected and focused into a photodiode detector. The scattered light flux is reasonable proportional to particle mass concentration.

A different approach has been reported in Germany – the TM-Digital (Armbruster and Breuer, 1983, pp. 689-699). This instrument has no pump and flow control system, the aerosols enters the sensing region due to the 'natural' convection in the air. Scattered light from a parallel beam of monochromatic infrared light is detected at an angle of 70° to the forward-facing direction.

In the TM-Digital instrument, sensing region is fully exposed to the total aerosol in the air monitored, which is a drawback compared to the SIMSLIN. This can lead to contamination of the optical surfaces by deposition of particles, resulting in drift if the instrument is used unattended over longer periods.

In the USA a corresponding instrument called Respirable Aerosol Monitor (RAM) exists. When used in combination with a cyclone pre-collector it is possible directly to measure the respirable fraction. By a pump the aerosol is lead through the cyclone, permitting only the respirable fraction to penetrate the optical sensing zone. Pulsed infrared light scattered in the angular range 45-90^{o} from the forward direction is then collected and detected by a photodiode detector. Photodiode signal is approximately proportional to the respirable aerosol mass concentration (Vincent, 1995).

A Mini-RAM (an extension of the RAM), has been developed. It is a passive device and like the TM-digital it responds to the respirable fraction. The instrument is small and can be used as a personal aerosol monitor.

Many such aerosol photometers, based on light scattering photometry are available. A more complete list is given in the ACGIH Handbook on air sampling instruments (Cohen and Hering, 1995).

The above mention RespiCon measures the particle concentration continuously and simultaneously for each of the three fractions, besides it collects the total number of each fraction on filters for later analysis.

8.2.10.4. Optical particle counters (light, lasers)

This technique is used for size distribution measurements. Particles are carried by an air stream through an illuminated viewing volume. The particles scatter the light, which is recorded by a photodetector. A voltage pulse is generated by the photodetector in response to each particle. The amplitude of the pulse is a measure of particle size diameter, which can be converted to the particle size distribution.

Counters using an incandescent light source are used for measuring size distributions in the range of 0.3 – 10 μm. By using lasers as light source, it is possible to measure size distributions down to as low as approximately 0.05 μm.

8.3. Determination of air volume

Accurate measurement of the air volume sampled is as important as an accurate determination of the sample quantity, because aerosol concentration is the ratio of the quantity sampled to the air volume sampled. Various methods exist, which can be classified into primary and secondary standards. Primary standards are those, which involve direct measurement of the

physical dimension of an enclosed volume, i.e. SI units. Secondary standards are meters, which can be traced by their calibration to a primary standard.

Table 16.

8.3.1. Primary standards

8.3.1.1. Spirometer

A spirometer is a cylindrical bell with its open end under water. The bell is balanced over a wheel with a counterweight. The volume entering the spirometer is determined by calculating the change in height times the bell's cross section.

8.3.1.2. Soap film flowmeter

In this flowmeter a soap film acts as an almost frictionless piston. The time it takes for the soap film to travel between two marks on the cylindrical tube is measured. The pumping rate is determined by dividing the volume between the two marks with the travelling time.

8.3.1.3. Pitot tube

Pitot tube is a primary standard for measuring gas velocity. Bernoulli's theorem applied to a Pitot tube in an air stream is:

$$v = \sqrt{\frac{2\ g\ P_V}{\rho_{Air}}} \tag{33}$$

where v is the linear velocity [$m \cdot s^{-1}$]. P_V the velocity pressure = total pressure minus static pressure [Pa]. g is the gravitational constant [$m \cdot s^{-2}$] and ρ_{Air} is the density [$kg \cdot m^{-3}$] of air. At STP the equation reduces to:

$$v = 1.2926\sqrt{P_V} \tag{34}$$

where the velocity pressure is measured in Pa.

When using a U-tube manometer, the accuracy of the pitot tube is satisfactory for velocities above approximately 13 $m \cdot s^{-1}$. At lower velocities an inclined manometer is needed.

Electronic capacitance pressure gauges permit measurements down to 0.5 $m \cdot s^{-1}$ (Cohen and Hering, 1995).

9.3.2. Secondary standards

8.3.2.1. Wet test meter

The wet test meter consists of a cylindrical container in which there is a partitioned drum, half submerged in water. The air enters at the centre of the cylinder, the flow of which makes the drum rotate. The rotation and thereby the volume are measured. When calibrated against a spirometer the accuracy is below 0.5% (Cohen and Hering, 1995).

8.3.2.2. Dry test meter

The dry test meter is similar to that used for domestic gas metering. It consists of two bags connected by mechanical valves. One bag is filled while the other is emptied. The meter is equipped with a cycle-counting device. Flow rates can be measured from 5 to 5000 $dm^3\ min^{-1}$ with an accuracy of 1%.

8.3.2.3. Electronic mass flowmeter

A unit consist of a heating element in a duct situated between two points where the temperature is measured. The temperature difference depends on the mass rate of the air and the heat input.

8.3.2.4. Laminar flowmeter

The pressure drop is directly proportional to the flow rate in the laminar flow type of variable-head meters. In commercial flowmeters laminar flow restrictors consist of egg-crate or tube bundle arrays of parallel channels. Alternatively a homemade kind of flowmeter can be constructed in the laboratory (Cohen and Hering, 1995) using cheap materials.

8.3.2.5. Fixed restricted flowmeters

This includes orifice and venturi meters and flow nozzles. If the flow in a closed channel is passing a fixed constriction it follows from Bernoulli's theorem that

$$W = q_1 \rho_1 = KYA_2 \rho_1 \left[2\sqrt{(P_1 - P_2)}\right] \qquad (35)$$

which apply for both orifice and venturi meters. W is the mass rate [$kg \cdot s^{-1}$], q_1 the volumetric flow at upstream pressure [$m^3 \cdot s^{-1}$] ρ_1 is density at upstream pressure, $K = C/(1-\beta^4)^{1/2}$, where C is the coefficient of discharge, dimensionless (Perry, 1984), β is the ratio of throat diameter to pipe diameter, dimensionless, Y is the expansion factor, dimensionless (Perry, 1984), A_2 is the cross-sectional area of the throat [m^2], P_1 is the upstream static pressure [Pa], and P_2 is the downstream static pressure [Pa]. This equation should be used with cautions, because it is sometimes difficult to determine the actual coefficient for a given system.

8.3.2.6. Orifice meter

An orifice meter should always be calibrated against a primary or secondary reference instrument.

8.3.2.7. Venturi meter

The Venturi meter minimizes the energy loss found in the orifice meters by using a converging (21 °) and diverging (5 – 15 °) cone before and after the orifice.

At STP, the flow Q [$dm^3\ min^{-1}$] can be calculated from:

$$Q = 5.897\ \beta^2\ D^2\ \sqrt{\Delta h} \tag{36}$$

where β^2 is the ratio of throat to pipe diameter, D the pipe diameter [cm], and Δh the difference pressure [Pa].

8.3.2.8. Rotameter

Rotameter are the most commonly used apparatus for metering volumetric airflow rates. They consist of a float, which is free to float up and down in a tube, which is wider at the top than in the bottom. The higher the airflow rate, the higher up the float will be. Accuracies down to 1-2% can be obtained, when the rotameters are calibrated in the system. A rotameter used must always be calibrated on the spot, because rotameters are very sensitive to differences in temperature and pressure (Cohen and Hering, 1995):

$$Q_{Site} = Q_{STP} \sqrt{\left(\frac{T_{Amb}}{T_{STD}}\right)\left(\frac{P_{STD}}{P_{Amb}}\right)\left(\frac{P_{Amb}}{P_{Rota}}\right)} \tag{37}$$

where $\underline{Q_{Site}}$ is the rotameter reading, $\underline{Q_{STP}}$ the flow rate at STP (20°C, 101325 Pa), $\underline{T_{Amb}}$ is the ambient temperature, $\underline{T_{STD}}$ is the standard temperature (293.15 K), $\underline{P_{STD}}$ is the standard pressure (101325 Pa), $\underline{P_{Amb}}$ is the ambient pressure on site [Pa], and $\underline{P_{Rota}}$ is the pressure at the rotameter inlet.

Correction is needed to correct for pressure drops over the sampler, high altitudes and temperatures deviating from 293.15 K.

At an elevation of 1524 m, the atmospheric pressure is only 83% of the pressure at sea level. If the temperature at site is 35 °C, the correction will be:

$$C_{Temp}\ C_{Altitude}\ C_{PressureDrop} = \sqrt{\left(\frac{273.15+35}{293.15}\right)\left(\frac{101325}{0.83\cdot 101325}\right)\left(\frac{0.83\cdot 101325}{0.83\cdot 101325-25000}\right)} = 1.025\cdot 1.098\cdot 1.196 = 35\% \quad (38)$$

for a pressure drop over the sampler of 25000 Pa. It is of note that at a temperature as high as 35 °C only increases the flow rate with 2.5 % and an elevation to 1524 m above sea level increases the flow rate with 9.76 %. The pressure drop over the sampler of 25000 Pa increases the flow rate with 15.2 % at sea level and 19.6 % at 1524 m.

8.3.2.9. Thermo anemometer

In a hot wire anemometer, the flow cools the sensor (a wire) proportional to the velocity of the air. Because the signals produced by the basic sensor are dependent on ambient temperature as well as air velocity, the probes are usually equipped with a reference element that provides an output, which is used for corrections. Some heated anemometers can measure velocities as low as 0.05 $m\cdot s^{-1}$ and as high as 40 $m\cdot s^{-1}$ (Cohen and Hering, 1995).

9. Discussions

In mines during excavation of minerals, during the building of houses, bridges, and roads, in many lines of manufacturing industry are workers exposed to airborne solid particles in the form of dust, smoke and fumes. Solid particles are created, e.g. by crushing, grinding, milling, and welding.

The dynamic behaviour of solid airborne particles, the size of which roughly ranges from 0.01 to 100 μm in diameters, has been described with a set of equations given in the method section of this paper. The mathematical manipulation of the equations has been kept at a minimum; instead transport properties are illustrated by a series of calculations for aerosols consisting of water, minerals, and uranium.

External forces due to gravimetric and electrostatic fields and gradients in temperature and concentration influence particles. Viscous forces act on particles when they are moving relative to the encompassing air.

When air experiences a laminar flow, the layers of air slide over each other. Turbulent flow is air which flow in eddies. At the workplace, transport is mainly due to turbulent eddies of air caused by movements of machines and vehicles, air moving due to heat radiation from machines, humans, and cold walls and windows. Further, wind may blow from open gateways, doors and windows.

Particles are removed from indoor air due to sedimentation and adhesion to the buildings surfaces. For large particles gravimetrical sedimentation is many order of magnitudes faster than deposition due to diffusion. For small particles deposition due to diffusion is dominating. A mineral particle with a diameter of 100 μm, falling from the ceiling of a six-meter high room, will in stagnant air reach the floor within 6.6 seconds. A one-μm particle will reach the floor after 16 hours and for a 0.01-μm particle it will take 334 days.

Number of particles in the air is reduced by particles agglomerating, leading to larger particles, with increased sedimentation velocity. Time to halve the number concentration is 30 μs for 1-μm particles, when the start concentration is 10^{20} particles per m^3, but when the start concentration is 10^8 it will take 343 days. When the start concentration is 10^{20}, will it take 208 μs to double the particle size, when the start concentration is 10^8, it takes 7 years. For the purpose of sampling, agglomeration may be ignored at number concentrations below 10^{12}.

The airflow in the human nose/mouth, the throat, and the bronchial region is turbulent, whereas the airflow in the alveoli is laminar. The small relaxation times for particles the short stopping distances indicate that deposition in the upper airways is mainly by impact for the particles with aerodynamic diameters above 10 μm. Particles with aerodynamic diameters

below 2.5 μm may reach the alveoli. The largest of the particles, which reach the alveoli, deposit due to gravity, the smallest deposit due to diffusion and action of electrical forces. The function of mass percent deposited as function of the aerodynamic diameter, therefore, passes though a minimum.

A single paper deals with the ability of occupational hygienist to assess aerosol concentrations by observation (Woitowitz et al., 1970, pp. 419-422). The conclusion of this paper was that it is not possible to assess exposure to aerosol by observation. If workers' exposure to solid particles, therefore, is to be assessed, the concentration of particles must be measured in the air they inhale.

The weak link in aerosol measurements is the sampling procedure, because no sampling devises can mimic the way human beings are breathing. Further, for the individual worker, the breathing pattern varies from day to day depending, e.g. on the workload and it varies between people. International conventions have established definition of the inhalable, the thoracic, and the alveolar fractions of an aerosol. The aim is that sampling devises should sample in accordance with these conventions.

Many sampling devises have been invented, which more or less comply with the given conventions, but their performance is not independent of the nature of the aerosol sampled. No single sampling equipment and no single procedure will be the best to use in all cases.

The range 0.01 – 100 μm is four decades. On a macroscopic scale four decade corresponds to 1 cm – 100 m. Obviously, a scale rule suitable to measure one cm would not be suitable for measuring 100 m. It is no wonder, therefore, that development of sampling devices which can cover four decades has been very difficult. Of six inhalable aerosol samplers tested, only one (RespiCon) was able to match the Inhalable Convention fairly, using monodisperse solid particles with aerodynamic diameters ranging from 5 to 68 μm. The other five samplers depended on wind speed, when wind speeds are above 0.5 m s^{-1}, wind direction, and particle size

The theoretical background given in this paper, the performance of the sampling devices considered, combined with knowledge about the nature of the aerosol and which compartment in the human airways is of concern, must, in each measurement situation, be judged separately. Help can be found, e.g. on the Internet. Useful World Wide Web addresses are given at the end of the reference list.

Occupational limit limits are based on mass. It is doubtful whether this measure of exposure in all cases is appropriate. Dose measured as number of particle deposited per day or surface area may sometime be more associated with risk. When sampling dust in which the

composition of toxic and/or radioactive varies with particle diameter, dose calculated on a mass basis is inappropriate.

10. Conclusions

Following statements about solid aerosols in general can be drawn:

- Man-made particles are created by different kinds of processes e.g. crushing, grinding, milling, using diesel-powered motors, and welding. Aerosols produced are typically with a diameter from 0.01 to 100μm.

- Particles are removed from the air due to sedimentation and adhesion to surfaces. Particles with aerodynamic diameter above 10 μm are mainly deposited due to gravity. Small particles with aerodynamic diameter below approximately 0.2 μm mainly deposit due to diffusion and action of electrical forces
  Number of particles in the air is reduced by agglomeration. This phenomenon may be ignored, when number concentrations are below 10^{12} particles per cubic meter.

- The air in the nose/mouth, the throat, and the bronchial region the air flow is turbulent, whereas the airflow in the alveoli is laminar

- Particles are inhaled and deposited in the different part of the human respiratory system due to the airflow patterns prevailing and the aerodynamic properties of the particles.

- Large particles (aerodynamic diameter > 10 μm) are deposited in the upper airways mainly due to impaction. The largest of the particles, which penetrate to the alveoli compartment (aerodynamic diameter 1 – 2.5 μm) deposit due to sedimentation, whereas the smallest particles (diameter 0.1 - 0.01 μm) mainly deposit due to diffusion and action of electrostatic forces.

- Sampling procedure of aerosols is a difficult task to handle. It has to mimic the breathing pattern of human beings as good as possible. Other components will influence and have to be considered for instance changes in breathing tempo and the nature of the aerosol sampled.

- International conventions are established for sampling of airborne particulates. Dose measured as number of particle deposited per day or surface area may sometime be more closely associated with risk than dose based on mass. If the dust sampled consists of particles the composition of which varies with size, dose calculated on a mass basis is inappropriate.

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APPENDICES

NOMENCLATURE

C_D Drag coefficient.

$C_D = 24/\mathrm{Re}$ for $\mathrm{Re} < 1$.

$$C_D = \frac{24}{\mathrm{Re}}\left(1 + \frac{\mathrm{Re}^{2/3}}{6}\right) \text{ for Re } \varepsilon\ [1, 1000].$$

$C_D \approx 0.44$ for Re ε [1000, $2 \cdot 10^5$]

$C_{Slip}(d)$ Slip correction factor. When small particles (d < 1 μm) settle, they do it faster than predicted by Stokes law, by a factor of $C_{Slip}(d)$, because there is a "slip" at the surface of the particles.

D Diffusion coefficient in air: Air = 1.99×10^{-5} $m^2 \cdot s^{-1}$ at STP (Hinds, 1999).

d_{Air} Diameter of air molecules at STP = 0.00037 μm (Hinds, 1999).

$d_{c\text{-}c}$ Collision diameter, distance between the centres of two particles at the instant of collision. Air: 3.7×10^{-10} m

$E_{Inhalable}$ Fraction of an aerosol, which will penetrate to the Exthoracic Compartment.

$E_{Thoracix}$ Fraction of an aerosol, which will penetrate to the Thoracic Compartment.

E_{Aveoli} Fraction of an aerosol, which will reach the Alveoli Compartment.

F_G Force due to gravity = $mg = m\ dv/dt$ [N]

F_{Drag} Force due to drag = $C_D\ \rho_{Air}\left(\frac{\pi}{4}\right) d^2\ v\ \phi / C_{Slip}(d)$ [N]

g Constant of gravity = 9.81 $m\ s^{-2}$

k Boltzmann's constant = R/N_A = 8.3143 $J \cdot K^{-1} \cdot mol^{-1} / 6.02 \times 10^{23}$ molcules mol^{-1} = 1.3811×10^{-23} $J \cdot K^{-1} \cdot molecule^{-1}$

M_{Air} 0.028964 Dalton ($kg \cdot mol^{-1}$)

m Mass of air molecules = M_{Air} / N_A = 0.029kg·$mole^{-1}$/6.02×10^{23} molecules·$mole^{-1}$ = 4.8×10^{-26} kg·$molecule^{-1}$

mfp Mean free path: the average distance travelled between successive collisions = $\frac{\bar{v}}{n_c} = \frac{1}{\sqrt{2}\ n \pi\ d_{c-c}^2}$.

For air at STP: $mfp_{Air} = 6.6 \times 10^{-8}$ m.

N Number of particles

N_A Advogados number: number of molecules in a mole = 6.02×10^{23} molecules·$mole^{-1}$

n Number of particles or molecules per m^3.

At STP: $n_{Air} = 2.5 \times 10^{25}$ molecules m^{-3}

n_c Number of collisions per second = $\sqrt{2}\, n\, \pi\, d_{c-c}^2\, \bar{v}$ [Collision s^{-1}]

P Pressure [Pa]

Re Reynolds number = $d\, v\, \rho / \mu$

Re_p Reynolds number for particle p = $d_p\, v_p\, \rho_p / \mu_{Air}$

STP One atmosphere (101325 Pa), 20 °C

u Random velocity [$m \cdot s^{-1}$]

u_{ms} Mean squared random velocity [$m \cdot s^{-1}$]

v Velocity [$m \cdot s^{-1}$]

$\bar{v}$ Mean molecular velocity = $\left(\frac{8kT}{\pi m}\right)^{0.5} = \left(\frac{8RT}{\pi M}\right)^{0.5}$

The molecular velocity of water vapours, CO_2, and air are 637, 407, and 503 $m \cdot s^{-1}$ at 20 °C, respectively (Hinds, 1999).

V Volume [m^3]

ϕ Form factor (= 1.00 for a sphere)

ρ Density [$kg \cdot m^{-3}$]

ρ_{Air} Density of air = 1.205 $kg \cdot m^{-3}$

ρ_p Density of particles: (1000 $kg \cdot m^{-3}$ (water), 3000 $kg \cdot m^{-3}$ (minerals), 18950 $kg \cdot m^{-3}$ (uranium))

ρ_{Air} Density of air at STP = 1.2041 $kg \cdot m^{-3}$

μ_{Air} Viscosity of air at STP = $\frac{2\,(m\,k\,T)^{0.5}}{3\,\pi^{1.5}\,d_{c-c}^2}$ = 1.81 10^{-5} Pa·s.

It is counter intuitive that viscosity of gases is independent of pressure, but this has been experimentally verified under pressures from 0.001 to 100 atmospheres (Hinds, 1999). Further, the viscosity of a gas increases with temperature, in contrast to the viscosity of a liquid.

List of tables

Table 1. Slip correction as function of particle diameter.

Table 2. Values of drag coefficients as function of Reynolds number.

Table 3. Shape factors.

Table 4. Relaxation time for particles as function of particle diameters.

Table 5. Sedimentation rates for spherical particles.

Table 6. Stop distance (inertial range) as function of particle diameter with initial velocity of 3.27 $m \cdot s^{-1}$.

Table 7. Some values of A, n and σ.

Table 8. Diffusion coefficient as function of particle diameter.

Table 9. Agglomeration coefficients K at STP *.

Table 10. Time for number concentration to halve and particle size to double for 1 μm mineral particles.

Table 11. Comparison of forces acting on particles.

Table 12. Cumulative deposition of unit-density particles from an aerosol onto a horizontal surface.

Table 13. Weibels model of the human airways.

Table 14. Percent deposited in the different compartments of the human airways.

Table 15. Common application of various types of filters. Advantages and disadvantages.

Table 16. Air sampling calibration methods.

TABLES:

Table 1. Slip correction as function of particle diameter

d [μm]	Slip correction $C(d)$
100	1.0015
10	1.0154
1	1.1546
0.1	2.9282
0.01	22.9764

Table 2. Values of drag coefficients as function of Reynold´s number (Re).

Re	Drag coefficient	Errors
< 1	24/Re	
1 – 1000	$\frac{24}{Re}\left(1+\frac{Re^{2/3}}{6}\right)$	Re from 3 to 400: 2% Re from 400 to 1000: 10%
1000 – 200000	0.44	

(Hinds, 1999).

Table 3. Shape factors

Types	Shape factor (ϕ)
Spheres [A)]	1.00
Cubes [B)]	1.08
Clusters of spheres [B)]	1.12 (2 chain)
	1.27 (3 chain)
	1.15 (3 chain compact)
	1.32 (4 chain)
	1.17 (4 chain compact)
Fibre (L/d=4) [A)]	1.32 (axis perpendicular to motion)
	1.07 (axis parallel to motion)
Bituminous coal [B)]	1.05-1.11
Sand [B)]	1.57
Quartz dust [A)]	1.36
Fused aluminium [A)]	1.04-1.49
Platelet shaped talc [A)]	2.04

[A)] (Vincent, 1995).

[B)] (Davies, 1979, pp. 477-513).

Shape factors are averaged over all orientations except where noted otherwise.

Table 4. Relaxation time for particles as function of particle diameters

d [μm]	Water τ[s]	Minerals τ[s]	Uranium τ[s]
100	3.07E-02	9.22E-02	5.83E-01
10	3.12E-04	9.35E-04	5.91E-03
1	3.54E-06	1.06E-05	6.72E-05
0.1	8.99E-08	2.70E-07	1.70E-06
0.01	7.05E-09	2.12E-08	1.34E-07

Table 5. Sedimentation rates for spherical particles

d [μm]	Water v_s [m s^{-1}]	Minerals v_s [m s^{-1}]	Uranium v_s [m s^{-1}]
100	3.02E-01	9.05E-01	5.71E+00
10	3.06E-03	9.17E-03	5.79E-02
1	3.48E-05	1.04E-04	6.59E-04
0.1	8.82E-07	2.65E-06	1.67E-05
0.01	6.92E-08	2.08E-07	1.31E-06

Table 6. Stop distance (inertial range) as function of particle diameter with initial velocity of 3.27 $m \cdot s^{-1}$

d [μm]	Water *s* [m]	Minerals *s* [m]	Uranium *s* [m]
100	1.01E-01	3.02E-01	1.90E+00
10	1.02E-03	3.06E-03	1.93E-02
1	1.16E-05	3.48E-05	2.20E-04
0.1	2.94E-07	8.82E-07	5.57E-06
0.01	2.31E-08	6.92E-08	4.37E-07

Table 7. Some values of A, n and σ

Industry		A Dimen-sionless	n Dimen-sionless	σ Charge/μm length
Jute	Batching	22.3	1.03	
	Spreading	27.8	0.80	
	Carding	28.6	1.19	
	Spinning	13.2	1.44	
	Winding	13.0	1.16	
Silica A		11.2	1.01	
Silica B		10.1	1.21	
Silica C		24.1	0.72	
Coalmine	Return roadway	25.0	1.20	
Asbestos 1.	Carding			13.0
	Spinning			10.1
	Weaving			9.6
Asbestos 2.	Carding			8.4
	Spinning (dry)			11.0
	Spinning /wet)			4.9
	Weaving			6.0

Table 8. Diffusion coefficient as function of particle diameter

d [μm]	Diffusion coefficient D [$m^2 s^{-1}$]
100	2.3751E-13
10	2.4081E-12
1	2.7382E-11
0.1	6.9442E-10
0.01	5.4488E-08

Table 9. Agglomeration coefficients K at STP

d [μm]	Correction Factor $\beta^{1)}$ Dimensionless	Agglomeration coefficient K^* $[m^3 \cdot s^{-1}]$	Corrected agglomeration coefficient K $[m^3 \cdot s^{-1}]$
100	1	2.98E-16	2.98E-16
10	0.99	3.03E-16	3.00E-16
1	0.97	3.44E-16	3.34E-16
0.1	0.82	8.73E-16	7.16E-16
0.01	0.14	6.85E-15	9.59E-16

* (Hinds, 1999)

Table 10. Time for number concentration to halve and particle size to double for 1 μm mineral particles

N_0 [ptc m^{-3}]	Mass concentration [mg·m^{-3}]	Time to reach 0.5 n_0		Time to double particle size	
10^{20}	1.57E+11	30	μs	208	μs
10^{18}	1.57E+09	3	ms	21	ms
10^{16}	1.57E+07	297	ms	2	s
10^{14}	1.57E+05	30	s	3	min
10^{12}	1.57E+03	49	min	6	h
10^{10}	1.57E+01	82	h	24	days
10^{8}	1.57E-01	343	days	7	years

Monodisperse spherical mineral particles, with a diameter of 1 μm, agglomerate into monodisperse, non-porous agglomerates. K = 3.37E-16 $m^3 \cdot s^{-1}$ see Table 9. ptc: particles.

Table 11. Comparison of forces acting on particles

	Forces [N]				
d_p [μm]	Adhesion[1)]	Gravity	Air current[2)]	Adhesion relative to gravity	Adhesion relative to air current
100	1.1E-05	1.5E-08	6.00E-07	7.1E+02	1.8E+01
10	1.1E-06	1.5E-11	3.00E-08	7.1E+04	3.6E+01
1	1.1E-07	1.5E-14	2.00E-09	7.1E+06	5.4E+01
0.1	1.1E-08	1.5E-17	1.50E-10	7.1E+08	7.3E+01
0.01	1.1E-09	1.5E-20	1.00E-11	7.1E+10	1.1E+02

[1)] predicted by: $F_{Adhesive} \approx 0.063\, d_p [1 + 0.009(\%RH)]$; where $\%RH$=50. [2)] v_{Air} = 10 m·s^{-1} (Hinds, 1999).

Table 12. Cumulative deposition of unit-density particles from an aerosol onto a horizontal surface

	Cumulative deposition		
d_p [μm]	Diffusion [ptc $m^{-2}s^{-1}$]	Settling [ptc $m^{-2}s^{-1}$]	Ratio diffusion/settling
100	5.50E-02	250000	2.20E-07
10	1.75E-01	3100	5.65E-05
1	5.93E-01	35	1.69E-02
0.4769	9.25E-01	9.245007	**1**
0.1	2.95E+00	0.85	3.47E+00
0.01	2.60E+01	6.9E-02	3.77E+02

Number concentration at $t = 0$: $n_0 = 10^6$ ptc m^{-3} (Hinds, 1999). ptc: particles.

Table 13. Weibel´s model of the human airways

Region	Generation	Number in generation	Diameter [cm]	Length [cm]	Volume [cm^3]	Mean air velocity [$cm\ s^{-1}$]
Throat	0	1	1.8	12	30.5	327
Extrathoracic bronchial region	1	2	1.22	4.76	11.0	356
Tracheobronchial region	5	32	0.35	1.07	3.0	271
	10	1024	0.13	0.46	6.2	61.5
Respiratory bronchial region	16	65500	0.06	0.17	30.5	4.75
Alveolar duct	23	8390000	0.04	0.05	554.0	0.075
Alveolar sacs	24	300000000	0.03	0.02	3200.0	0.001

(Weibel, 1963). In the first 16 generation the airflow is turbulent. After the 17-18 generation the airflow is laminar (Schneider, 1996). The air velocity is given for a tidal volume of 1450 cm^3 (Schneider, 1996). In Table 13, the ciliated compartments are shaded.

Table 14. Percent deposited in the different compartments of the human airways

d_{Ae} μm	Not inhaled	Inhaled Convention	Thoracic Convention	Alveoli Convention	Deposited in exthoracic compartment	Deposited in thoracic compartment	Exhaled	Deposited in the alveoli
100	49.88	50.12	0.00	0.00	50.12	0.00	0.00	0.00
10	22.56	77.44	49.67	1.31	27.77	48.36	0.00	1.31
2.5	6.96	93.04	93.03	83.38	0.01	9.65	65.12	18.25
1	2.91	97.09	97.09	97.06	0.00	0.03	75.73	21.33
0.1	0.30	99.70	99.70	99.70	0.00	0.00	69.79	29.91
0.0 1	0.03	99.97	99.97	99.97	0.00	0.00	67.98	31.99

(Vincent, 1995).

Table 15. Common application of various types of filters. Advantages and disadvantages

Filter type	Application	Advantages	Disadvantages
Membrane filters	sub-micron particle collection	High loading efficiency High mechanical strength	High pressure drop Rapid clogging
Cellulose Mixed esters nitrate, acetate, etc. and PVC	Sampling of metal, cotton dust, asbestos, etc. in NIOSH standard methods	Cheap Low chemical resistance	Hygroscopic Electrostatic charge build-up in PVC membranes
Teflon membranes	Gravimetric analysis, neutron activity analysis	Inert to chemicals non-hygroscopic Low blind value	Loss of nitrates observed
Silver membranes	Organic particulate collection and analysis.	Chemical resistant Low blind value	Very expensive

Table 16. Air sampling calibration methods

Type of meter	Quantity measured	Range
Spirometer	Integrated volume	6 – 600 dm^3
Soap film flowmeter	Integrated volume	2 – 10000 cm^3
Wet test meter	Integrated volume	0.5 – 230 $dm^3\ min^{-1}$
Dry test meter	Integrated volume	10 – 150 $dm^3\ min^{-1}$
Electronic mass flowmeter	Mass flow rate	0 – 3000 $dm^3\ min^{-1}$
Laminar flowmeter	Volumetric flow rate	0.02 $cm^3\ m^{-1}$ – 1.0 $m^3\ min^{-1}$
Venturi meter	Volumetric flow rate	Depends on pipe and orifice diameters
Orifice meter	Volumetric flow rate	Depends on pipe and orifice diameters
Rotameter	Volumetric flow rate	from 1 $cm^3\ min^{-1}$ up
Thermo anemometer	Velocity	from 0.3 m min^{-1} up
Pitot tube	Velocity	from 300 m min^{-1} up

(Cohen and Hering, 1995)

Figure Captions

Figure 1. Particle sizes of some aerosols (after (Hinds, 1999), (Vincent, 1995), (Evans et al., 1999)).

Figure 2. Mean free path: The larger particles experience the air as a continuum, in contrast to smaller particles. Mean diameter of air molecules: 0.00037 μm, Approximately molecular spacing: 0.004 μm. Mean free path in air: 0.066 μm. pct: particle

Figure 3. Sedimentation of particles. m: mass of particle, g: the constant of gravity, v(t): velocity at time t, F_D: drag force. d: diameter of particle. μ_{Air}: viscosity of air. $C_{Slip}(d)$: Cunningham's slip factor. τ: relaxation time.

Figur 4. The human airways (Purves et al., 1995)

Figure 5. From irregular shape to aerodynamic particle (Hinds, 1999). d_p: particle diameter. d_V: particle diameter of a equivalent spherical particle. d_{Ae}: aerodynamic diameter. ρ: particle density. v_s: sediment velocity. m: particle mass, g: constant of gravity.

Figure 6. International Conventions on aerosols (European Commitee for Standardization (CEN), 1993)

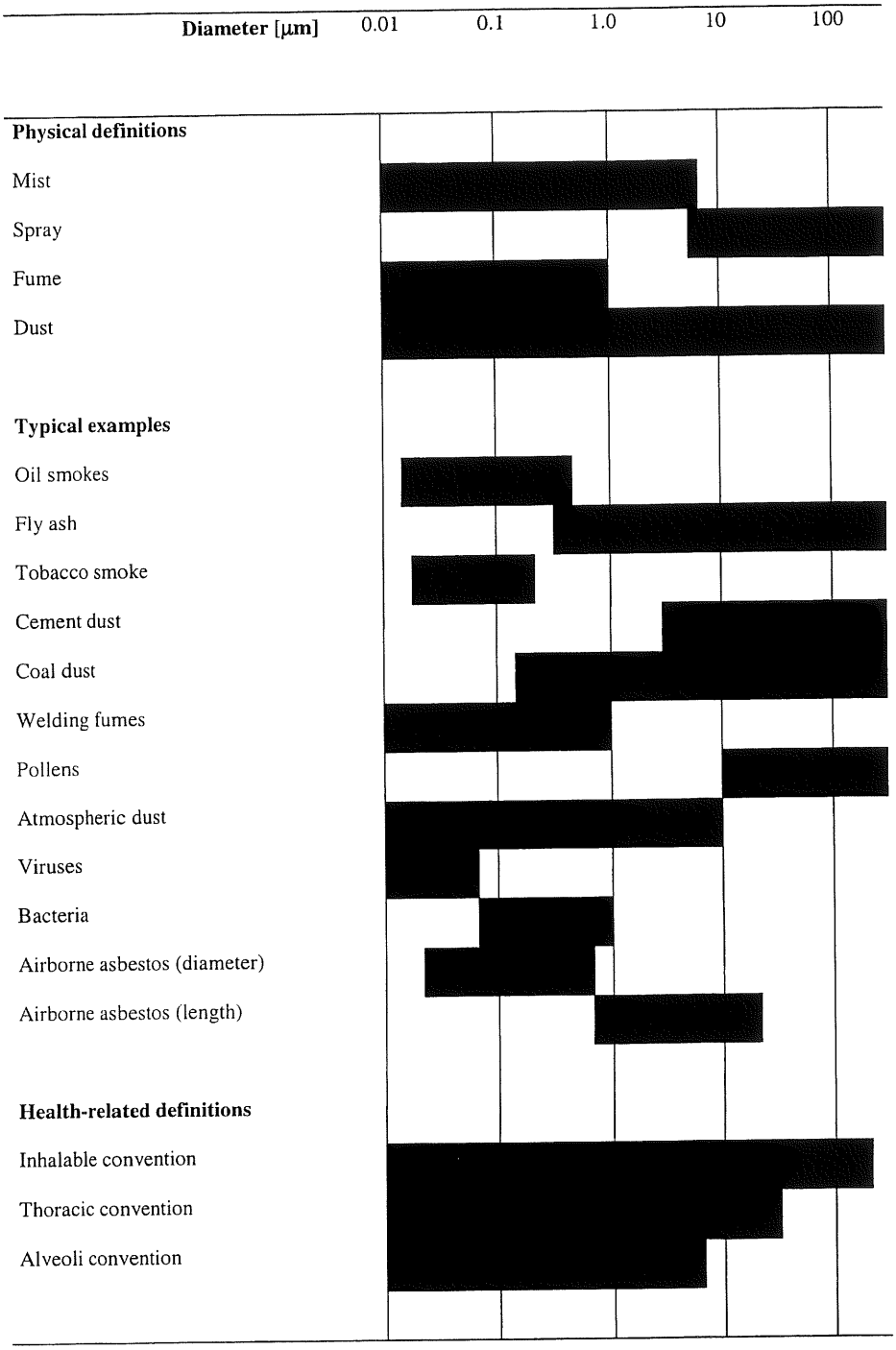

Diameter [µm]
0.01
0.1
1.0
10
100
Physical definitions
Mist
Spray
Fume
Dust
Typical examples
Oil smokes
Fly ash
Tobacco smoke
Cement dust
Coal dust
Welding fumes
Pollens
Atmospheric dust
Viruses
Bacteria
Airborne asbestos (diameter)
Airborne asbestos (length)
Health-related definitions
Inhalable convention
Thoracic convention
Alveoli convention

Figure 1.

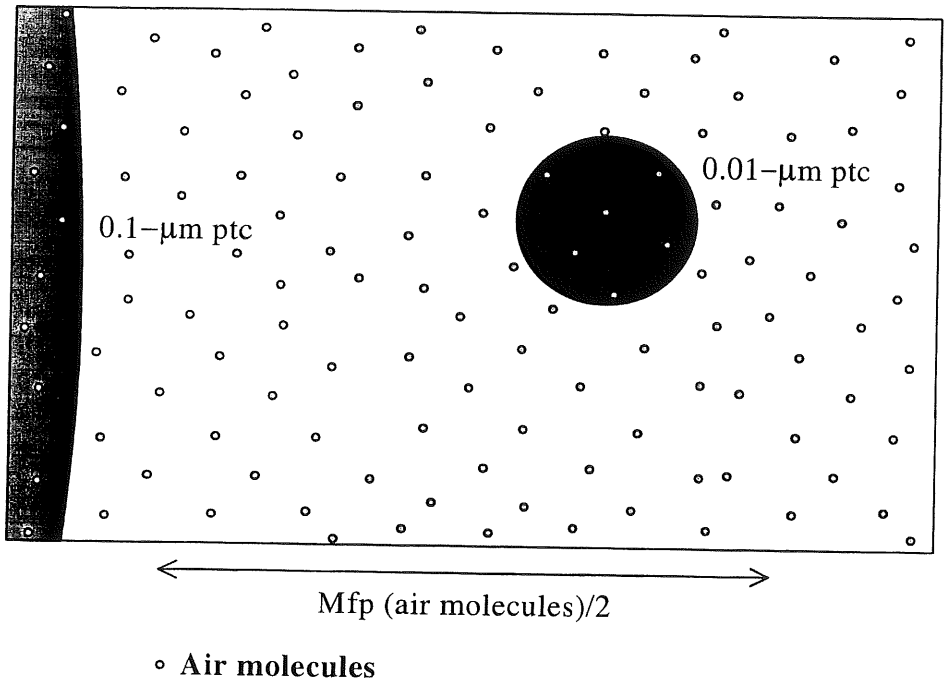


Figure 2.

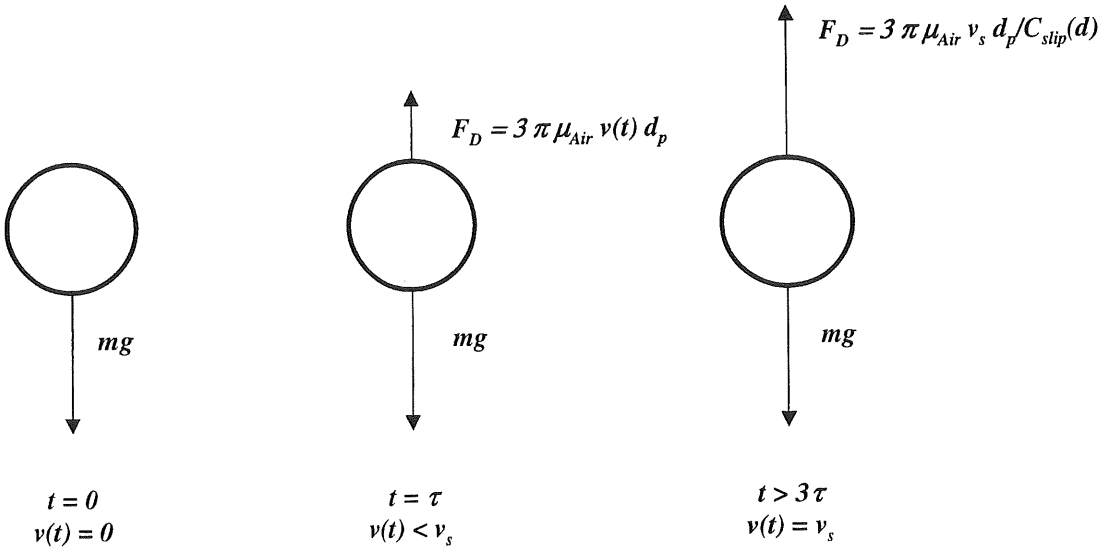
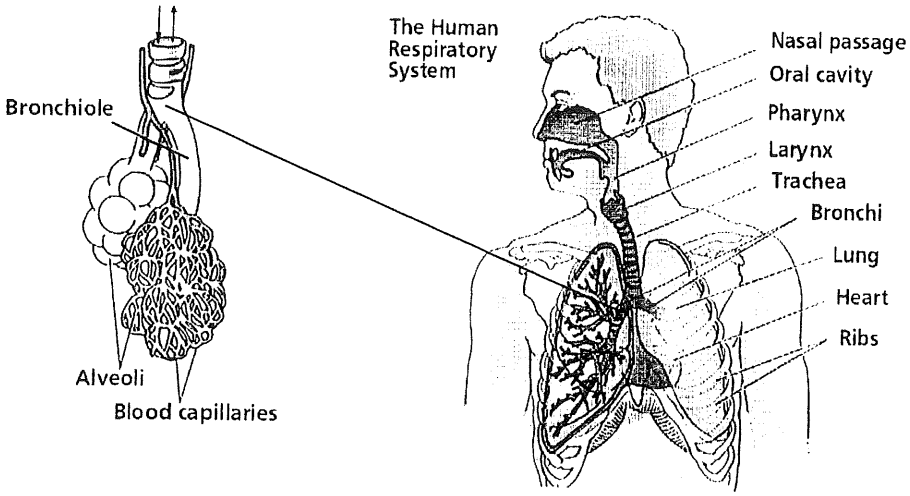

$F_D = 3\pi\mu_{Air} v_s d_p/C_{slip}(d)$
$F_D = 3\pi\mu_{Air} v(t) d_p$
mg
mg
mg
$t = 0$
$v(t) = 0$
$t = \tau$
$v(t) < v_s$
$t > 3\tau$
$v(t) = v_s$

Figure 3.


The Human
Respiratory
System
Bronchiole
Alveoli
Blood capillaries
Nasal passage
Oral cavity
Pharynx
Larynx
Trachea
Bronchi
Lung
Heart
Ribs

Figur 4.

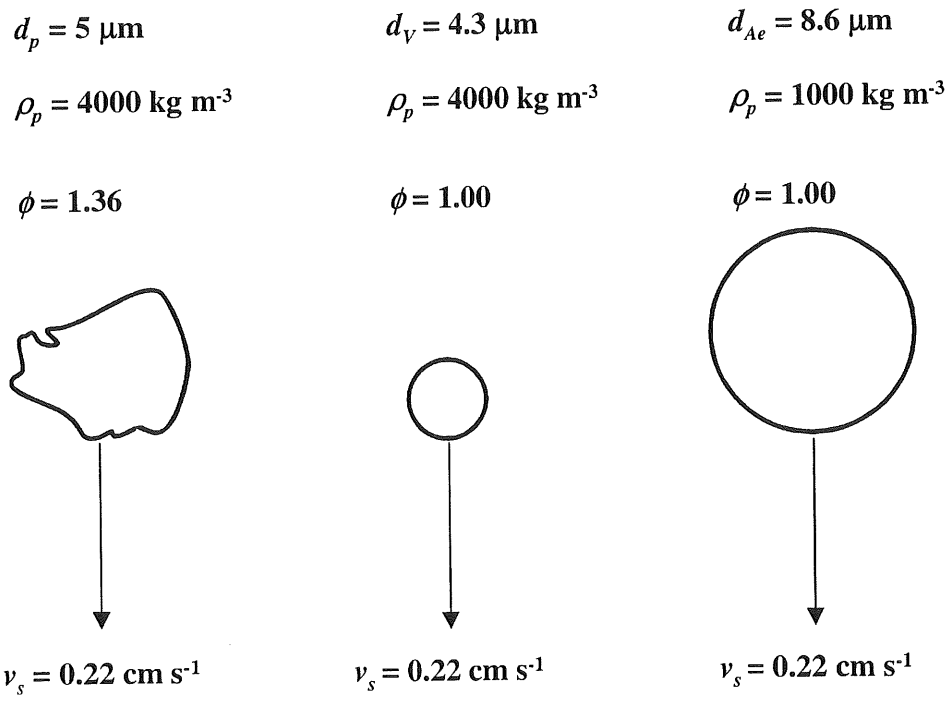

d_p = 5 μm
ρ_p = 4000 kg m^{-3}
ϕ = 1.36
v_s = 0.22 cm s^{-1}
d_V = 4.3 μm
ρ_p = 4000 kg m^{-3}
ϕ = 1.00
v_s = 0.22 cm s^{-1}
d_{Ae} = 8.6 μm
ρ_p = 1000 kg m^{-3}
ϕ = 1.00
v_s = 0.22 cm s^{-1}

Figure 5.

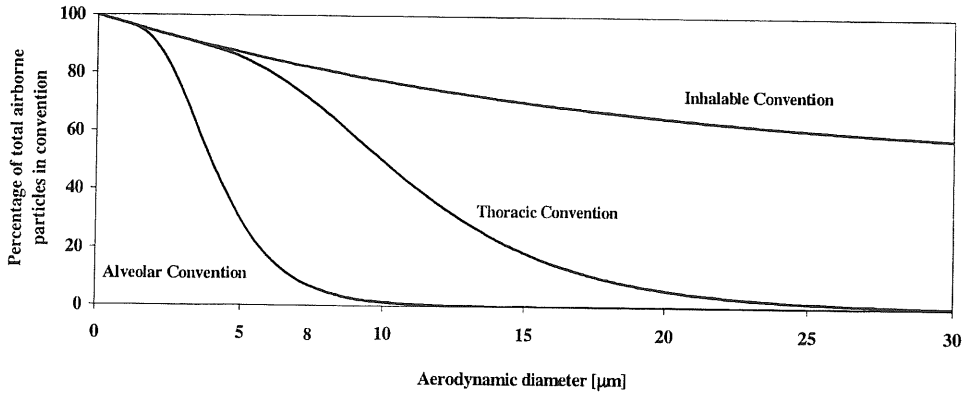

Percentage of total airborne particles in convention
100
80
60
40
20
0
Inhalable Convention
Thoracic Convention
Alveolar Convention
0
5
8
10
15
20
25
30
Aerodynamic diameter [µm]

Figure 6.

Paper [C]

QUANTIFYING EXPOSURE TO AIRBORNE STYRENE AND THE ASSOCIATED UNCERTAINTY DEPENDING ON THE SAMPLING STRATEGY APPLIED

[C] QUANTIFYING EXPOSURE TO AIRBORNE STYRENE AND THE ASSOCIATED UNCERTAINTY DEPENDING ON THE SAMPLING STRATEGY APPLIED

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ABSTRACT

During the last decade a measurement strategy proposed by Rappaport, in the present paper referred to as Strategy 1 (Rappaport, 1991; Rappaport *et al.*, 1995; Rappaport *et al.*, 1999), has become the most commonly applied measurement strategy to obtain unbiased data for exposure assessments. In 1994 another approach, the logbook method (referred to as Strategy 2), to obtain unbiased data for exposure assessment was proposed (Olsen, 1994). An extended version of the logbook method, Strategy 3, is proposed and applied in the present paper. Traditionally new methods are validated against well known, well tested methods. In the present thesis the new measurement strategy (Strategy 3) is thus validated, tested and compared to the measurement strategies Strategy 1 and Strategy 2. A study is done in which all three strategies are applied to obtain a unique dataset to be used for comparison of the strategies and their usefulness are considered.

The average daily exposure (8h TWA) to styrene for single workers, working in a windmill wing plant, is estimated and the associated uncertainty quantified. The uncertainty depends on the sampling strategy applied. Subsequently, major exposure sources are identified and quantified to be used for intervention.

It is concluded that all strategies applied provide information on exposure at group level. 8h TWA of a single day is estimated more precise under Strategy 1, but the value of the long-term average daily exposure at the individual level is more accurate estimated applying Strategy 2 and Strategy 3. In addition, Strategy 2 and Strategy 3 provide quantitative information useful for decisions making on interventions to control, reduce or eliminate exposure. Under Strategy 3 the estimated **PC**s have uncertainties of the same magnitude as **PC**s measured. There is an economic benefit in applying Strategy 3 compared to the traditional logbook method (Strategy 2) because the consumption of occupational hygienist time can be reduced. Strategy 3 therefore is adequate as a screening method and sampling can be done by workers themselves (SAE).

Keywords: Sampling strategy, styrene, exposure assessment, exposure modelling

INTRODUCTION

Styrene is used as a cross linking agent primary in the fibreglass reinforced polyester, glue and rubber industry. It is one of the most widely used monomers mainly in the production of polystyrene and co-polymeric products such as acrylonitrile-butadiene-styrene resins, styrene-butadiene rubbers, latexes and unsaturated polystyrene resins (IARC, 1994).

Styrene is classified by the International Agency for Research on Cancer (IARC) as *possibly carcinogen to humans (2B)* (IARC, 1994). Styrene is primary absorbed in humans by inhalation (60-70%) or by dermal transfer. At present, data obtained from epidemiological data are inadequate to establish a direct cause and effect relationship between exposure for styrene and cancer in humans. Styrene has effects on the neurological system as volatile organic compounds in general. Common symptoms are depression, concentration problems, fatigue and nausea. Styrene vapour may also lead to irritation of eyes, nose and throat. It is indicated that styrene has an effect on reproduction as well, but appropriate data lacks (Gezondheidsraad, 2001). It has been shown that exposure to styrene even in lower concentrations (50-100 mg m^{-3}) can cause adverse effects on health (Vaino *et al.*, 1977).

Occupational exposure levels, measured both by air measurements and biological monitoring have been highest in the manufacture of fibre glass-reinforced polyester products (exposure to airborne styrene: 40-400 mg m^{-3}) and lower in the production of styrene, polystyrene and styrene-based plastics and rubbers. In most parts of the industry in general, the level of occupational exposure to airborne styrene has been found to be modest (<10 mg m^{-3}) (IARC, 1994). The limit value for styrene in Denmark is 25 ppm (cm^3 m^{-3}) or 106 mg m^{-3} (Anon.2000). It is a ceiling limit, which should never be exceeded. Styrene is a component in cigarette smoke and automobile exhaust and in low levels it may occur naturally as well in foods (Johanson *et al.*, 2000). It is a colourless liquid with a characteristic, distinct odour, which can be smelled even at extremely low concentration levels.

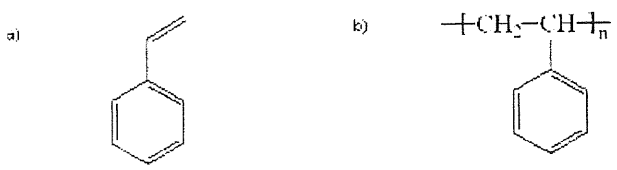


Figure 1. Molecular structures of styrene (a) and polystyrene (b)

The main purpose of measuring exposure to a contaminant in the working environment is to secure that exposure concentration is well below a level, considered to protect the workers (OEL). Contaminants causing adverse health effects due to long-term exposure should be measured as the long-term arithmetic mean exposure, because this value can be related to the risk of adverse health effects due to chronic exposure for the single worker (Rappaport, 1991). Another purpose could be to collect data, to form the basis for decisions on where and how to intervene to improve the working environment when needed.

The purpose of the exposure assessment determines the choice of a sampling strategy. One purpose could be to estimate the exposure distribution of the arithmetic mean (AM) of a group over time, a strategy appropriate for epidemiological studies. Another strategy could be to estimate the average exposure of individuals and compare this value to average exposures of e.g. other persons. This strategy is suitable for studies in occupational hygiene for improving the working environment under limited resources or determining compliance with OELs. In this paper three strategies are considered.

OBJECTIVES

The objective of this study is to quantify and compare estimations of exposure ($\bar{x} \pm U$) of individual workers and the associated uncertainty, depending on sampling strategy applied. Subsequently major exposure sources are identified to be used for intervention.

Three unbiased, sampling strategies for which workers are randomly selected, are applied:

1. Strategy 1: Measured 8 hours time weighed average concentrations (8h-TWA) (Lyles *et al.*, 1997; Nylander-French *et al.*, 1999; Rappaport *et al.*, 1993; Rappaport *et al.*, 1995; Rappaport *et al.*, 1999), in the present paper referred to as 'the measured 8h-TWA strategy' or Strategy 1.
2. Strategy 2: Logbooks plus measured process concentrations (**PC**s) followed by calculation of 8h-TWA (Olsen, 1994; Olsen *et al.*, 2002) in the present paper referred to as 'the logbook method (**PC**)' or Strategy 2.
3. Strategy 3: Logbook plus measured 8h-TWAs followed by calculation of **PC**s (Nyeland *et al.*, 2002b) in the present paper referred to as 'the logbook method (8h-TWA)' or Strategy 3.

Data obtained under the different sampling strategies are compared.

SAMPLING STRATEGIES

Methods for estimating exposure: $\bar{x} \pm U$.
Unbiased sampling strategies, random selection of workers.

Different kinds of strategies depending on the purpose can be applied in quantitative exposure assessment. One approach is to estimate exposure at the individual level. A second approach is to estimate the average level of a group's exposure, to be applied to all members of the group. In this case only a representative sample of the group are being sampled.

In the present study three unbiased sampling strategies are applied in which workers are selected by simple random selection. The goal is to estimate the long-term arithmetic mean exposure for a single worker, because this measure can be related to the risk of adverse health effects (Rappaport, 1991).

Table 1. Three unbiased sampling strategies to be applied for exposure assessments

Name of strategy	To be used for:	Technique	Measurements
Strategy 1: 'Measured 8h-TWA'	Epidemiological use. Useful for control of exposure of a group.	Estimating the average exposure of a group of workers over time. Distribution of mean exposures of individuals.	8h TWA Repeated measurements
Strategy 2: Logbook method (**PC**)	Individual control of exposure. Identification and quantification of sources for intervention improvements. Epidemiological use.	Estimating the average exposure of individuals over time.	Logbook + **PC**s for calculating 8h TWA
Strategy 3: Logbook method (8h-TWA)	The same as Strategy 2 Screening	The same as Strategy 2	Logbook + 8h TWA for calculating **PC**s

8h TWA is the Time-Weighted Average of concentration for a 8-hour workday. 8h TWA measurements do not necessarily mean that measurements have been carried out for exactly 8 hours. Usually the measurement period is less, about 5-7 hours, expected to reflect exposure through the intire working day.

Strategy 1: 'Measured 8h-TWA' strategy

A random selection of people can be stratified on the base of homogeneous exposure groups (HEG) or similar exposure groups (SEG) (Mulhausen *et al.*, 1998; Rappaport, 1991). The population investigated is divided into groups supposed to be exposed to approximately the same mean concentration level. Criteria for this classification could for instance be that the workers have the same job titles, are exposed to the same agents or that they are working in similar surroundings with the same kind of ventilation. Often it is seen that such HEGs are inhomogeneous (Rappaport *et al.*, 1993).

A method using random sampling for collecting data was proposed by Rappaport (Rappaport *et al.*, 1995) in the present paper referred to as Strategy 1. Data are analysed using the random effects model (model 1) (Lyles *et al.*, 1997; Rappaport *et al.*, 1995) or with explanatory variables such as process- and task-related covariates using mixed models (model 2) (Nylander-French *et al.*, 1999; Peretz *et al.*, 2002; Rappaport *et al.*, 1999).

Measurements can be performed as 8-hour measurements, handled by the workers themselves SAE*, (Self-Assessment of Exposure), distributed and collected by mail (Liljelind *et al.*, 2000; Rappaport *et al.*, 1999). It is possible to estimate the average within- and between-worker variations, when at least two measurements on each worker are carried out. Covariates such as ventilation (LEV/natural ventilation), continued/intermittent work patterns, working indoor/outdoor, etc. contributing to exposure, can be identified and investigated at a general level.

Statistical models of Strategy 1 are shown below:

MODEL 1: $Y_{ij} = ln(X_{ij}) = \mu_y + \beta_i + \varepsilon_{ij}$

MODEL 2: $Y_{h(ij)} = ln(X_{h(ij)}) = \mu_y + \alpha_h + \sum \delta_m C_{mh(ij)} + \beta_{h(i)} + \varepsilon_{h(ij)}$

- X_{ij} - Exposure level on the j-th day for the i-th worker
- $X_{h(ij)}$ - Exposure level on the j-th day for the i-th worker in the h-th job
- μ_y - The underlying, mean exposure level over all jobs
- α_h - The fixed effect of the h-th job $\sum \alpha_h = 0$
- $\sum \delta_m C_{mh(ij)}$ - Additional fixed effects for task- and process-related covariates (m=1,2,3....p) where the regression coefficients $\delta_1, \delta_2, \delta_3 \ldots \delta_p$ represents the fixed effects of the p covariates
- $\beta(i)$ - The random effect of the i-th worker (~iid; $N(0,\sigma^2_B)$)
- $\varepsilon(ij)$ - The random effect of the j-th day for the i-th worker (~iid; $N(0,\sigma^2_W)$)
- $\beta_h(i)$ - The random effect of the i-th worker (~iid; $N(0,\sigma^2_B)$)
- $\varepsilon_h(ij)$ - The random effect of the j-th day for the i-th worker (~iid; $N(0,\sigma^2_W)$)

* SAE is not a suitable name for this kind of sampling. Workers are not doing any *assessment* - more correctly they are doing *sampling*.

Data from measurements are log transformed i.e. exposure is assumed to be lognormal distributed. Effects in the model are assumed to act multiplicatively on exposure level due to that it is exposure of the group that is modelled.

Measurement method: Measurements can be performed as 8-hour measurements, SAE (Self-Assessment of Exposure), handled by the workers themselves, distributed and collected by mail. Recently it has been shown that unbiased exposure data were collected by workers themselves using this measurement method (Liljelind *et al.*, 2001). Time for opening and closing the tube are noted. There is no need for the occupational hygienist to be present.

Strategy 2: The logbook method (PC measured)

An alternative strategy is the logbook method (Olsen, 1994), where exposure concentration and exposure time are measured separately. The Process Concentration (**PC**) for each process is estimated, by measuring different operators while they perform the process. Exposure time is measured by workers keeping logs on when they start and stop different processes during the logbook period. A matrix for daily exposure concentration for each worker can be established, based on **PC** for each process performed during working days and the exposure time (Δt_p).

Stratifying on the base of processes often results in a reduction of the variability in data (Olsen, 1994). A higher degree of accuracy on the measurement result (a workers long-term arithmetic mean exposure) is obtained, because a larger number of estimates for daily exposures are obtained applying Strategy 2. The logbook method is based on process domain and time measurements (logbook) on the contrary to Strategy 1, in which exposure is measured in time domain (Olsen, 1994). Exposure estimates at the individual as well as at the population level are obtained applying the logbook method.

The following matrix of each worker can be established in which each raw is a day in the log period and P_j is processes:

MODEL:

$$C_{Day1} = f_{P1,\,Day1}\ PC_{P1} + f_{P2,\,Day1}\ PC_{P2} + ...$$

$$C_{Day2} = f_{P1,\,Day2}\ PC_{P1} + f_{P2,\,Day2}\ PC_{P2} + ...$$

.....

$$C_{Day\,i} = f_{P1,\,Day\,i}\ PC_{P1} + f_{P2,\,Day\,i}\ PC_{P2} + ...$$

$C_{Day\,i}$	-	the time-weighed average (TWA) concentration of pollutant during working day *i*.
$f_{Pj,Day\,i}$	-	the fraction of day *i*, during which process *j* is performed.
PC_{Pj}	-	the process concentration (**PC**) of the *j*'th process.

The process concentration (**PC**) is calculated as:

$$PC = \bar{C}_{Pj} = \frac{1}{N}\sum_{n=1}^{N} C_{Pj\,n}$$

P_j	-	process *j*
N	-	number of measurements
n = index		

A mean value for 8h day measurements of individual workers during the logbook period can be estimated.

Measurement method: **PC** measurements are performed by the occupational hygienist measuring several times on the same or different operators performing the same process. Measurement period is about 10-15 minutes. Active personal sampling is often used to collect enough of agent on tubes for analysis. Time measurements are recorded in logbooks by workers.

Strategy 3: The logbook method (8h-TWA measured)

A measurement method, based on the logbook method, using 8h TWA measurements to estimate **PC**s is proposed by Nyeland et al. (Nyeland *et al.*, 2002b) and applied in the present paper. Passive personal sampling is done over approximately 8 hours. The need for an occupational hygienist present during sampling is thus reduced or eliminated in principle compared to Strategy 2. Applying this version of the logbook method, it is possible to calculate **PC**s from 8h TWA measurements and logbooks.

The matrix consisting of time measurements from the logbooks and 8h TWA measurements as C_{Dayi}-values, values for the different process concentrations (PC_{Pj}) can be estimated by solving the matrix system as a general linear model. In order to be able to separate the individual process concentrations, time spent at different processes should preferably be such that the columns in the logbook-matrix are linearly independent. To obtain reliable estimates for the individual process concentrations, larger amounts of data are needed compared to Strategy 2. The method is thus suited for larger studies.

When **PC** of all processes have been estimated based on 8h TWA measurements, the 'traditional' logbook method can be used to calculate 8h TWAs to estimate individual long-term exposures for workers on an even larger scale, based on logbooks and estimated **PC**s.

Measurement method: 8h TWA measurements are collected most efficiently using passive sampling, which is a method easily handled by workers themselves as described above. The need for an occupational hygienist is thus eliminated, compared to the logbook method in which **PC**s are measured. A name for this version of Strategy 3 is 'The WSS-Logbook method' (Workers Self-Sampling).

Exposure estimated applying the logbook methods can be described in a more general statistical model to be investigated using mixed models. As the contributions from individual process concentrations are integrated during the working day, an additive model for the measurements has been chosen. The residual variation is modelled by a normal distribution. As the major source of variation in daily exposures is caused by the explained variation in work patterns and process concentrations, this model is not in conflict with the usual lognormal model for overall variation of daily exposures of workers in the occupational environment.

MODEL: $X_{h(ij)} = \mu_y + \alpha_h + \sum_{m=1}^{m=p} f_m C_{mh(ij)} + \beta_{h(i)} + \varepsilon_{h(ij)}$

$X_{h(ij)}$	-	Exposure level on the j-th day for the i-th worker in the h-th job
μ_y	-	The underlying, mean exposure level over all jobs
α_h	-	The fixed effect of the h-th job or department $\Sigma\, \alpha_h=0$
$\sum_{m=1}^{m=p} f_m C_{mh(ij)}$	-	Where the regression coefficient f_m (the fraction of time spent at m process during a working day), represents the fixed effects of the covariates, C_m, (m=1,2,3...p) (the processes performed) on the j-th day, based on the logbook filled in by the i-th worker.
$\beta_{h(i)}$	-	The random effect of the i-th worker (~iid; N (0, $\sigma^2_{B,h}$)
$\varepsilon_{h(ij)}$	-	The random effect of the j-th day for the i-th worker (~iid; N (0,$\sigma^2_{W,h}$)

The obtained, estimated values for process concentration could be used for further estimation of individual long-term exposures for workers just by filling in logbooks. There is a huge economic benefit in using the logbook methods because the need for measurements is reduced or eliminated. Exposure assessments can be conducted prospectively based on the exposure model obtained for individual workers and work patterns can be changed even before exposure has occurred. When implementing an exposure model in one company based on data from another company it will be necessary to validate the model, based on new measurements.

Applying the logbook methods (Strategy 2 or Strategy 3), individual short-term and long-term exposure levels can be estimated together with day-to-day variation in exposure. They are appropriate to provide quantitative information on where to intervene to reduce exposure. Processes resulting in the highest concentration (short-term exposure) as well as highest dose (long-term exposure) can be identified.

Uncertainty estimation for measurement procedure and exposure concentration

A way to list and quantify all possible uncertainty components through sampling and analysis leading to a result, is to make an uncertainty budget. Usually uncertainty budgets are made only for the sampling procedure and analysis of the sample. Uncertainty due to these steps have recently been evaluated and quantified according to the procedure described in the Guide to the Expression of Uncertainty in Measurement (GUM)(BIPM, 1993) for measuring concentration of airborne styrene in workers breathing zone (Nyeland *et al.*, 2002a). It is possible to include uncertainty due to sampling strategy applied as a higher level in the uncertainty budget, in case sampling has been performed in an appropriate manner as in the present study.

In the present paper the vision of the strategies applied are to estimate the long-term arithmetic mean exposure of a single worker, because it is the measure of exposure, which can be related to risk of adverse health effects due to chronic exposure (Rappaport, 1991). The final measurement result is thus the persons mean 8h TWA of exposure as illustrated by the flow diagram in Figure 2. When estimating uncertainty due to the sampling strategy applied, uncertainties from all other levels in the flow diagram have to be quantified. Uncertainty in estimating process concentration of exposure to styrene in air, when using the logbook method, has been quantified, using an uncertainty budget (Nyeland *et al.*, 2002a).

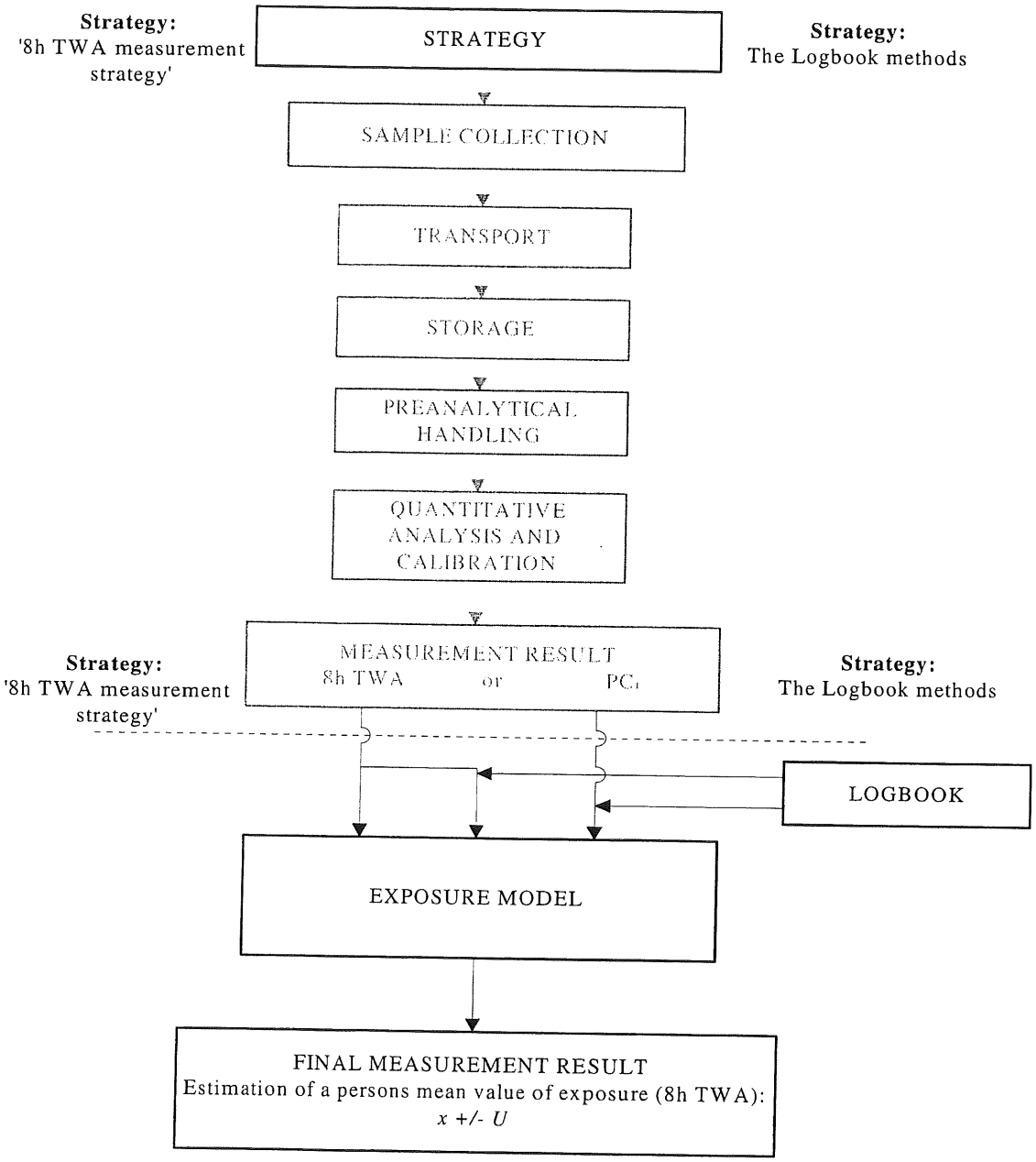


Figure 2. Flow diagram of the procedure for estimating exposure to styrene, under different strategies. Levels considered in the present paper are highlighted. The other levels are estimated by Nyeland et al. (Nyeland *et al.*, 2002a).

In the present study, data for estimating exposure to styrene in a windmill wing factory are collected applying three sampling strategies, Strategy 1, Strategy 2 and Strategy 3, leading to the following measurements:

- Strategy 1 ('Measured 8h TWA strategy') → 8h TWAs
- Strategy 2 (The logbook method (logbooks + **PC**s measured)) → 8h TWAs
- Strategy 3 (The logbook method (logbooks + 8h TWAs measured)) → **PC**s
  Subsequently applied in larger scale:
  (logbooks + PC calculated) → 8hTWAs

Data obtained can be used for comparing the uncertainty on estimation of the individual arithmetic mean exposure, depending on sampling strategy applied. Data obtained applying Strategy 2 and Strategy 3 provides information to identify major exposure sources.

MATERIALS AND METHODS

Study population

For the present study, a factory in the fibreglass reinforced polyester industry, producing windmill wings was selected among companies in the Danish reinforced plastics industry. The factory is modern, well equipped and with good ventilation facilities. A total of 450 employees.

367 workers working in 3 separate departments (Hall I and II - 12 hrs day- and nightshift, Hall III - 8 hrs dayshift) were included in the study. Range of age was between 19 and 61 years. Table 2 shows how they are distributed in the 3 departments.

Table 2. The distribution of workers in departments.

Department	Shift 1 (12 hrs)		Shift 2 (12 hrs)		Shift 3(8hrs)
	Day (D1)	Night (N1)	Day (D2)	Night (N2)	Day (D)
Hall I	20 (F) 43 (M)	10 (F) 72 (M)	19 (F) 57 (M)	17 (F) 59 (M)	
Hall II	1 (F) 9 (M)	- 8 (M)	1(F) 10 (M)	- 4 (M)	
Hall III					34 (F) 3 (M)

F – female; M – male.

The production in the departments

Different parts of the windmill wings were produced in the three halls investigated.

Hall I: Start of the production. 10 forms were placed in Hall I. Each form consists of two parts. The wings are cast in the forms, starting with gel coating (spray painting in the form, which is the outer layer of painting on the wing using a product including styrene) as the first step. Then a layer of glass web is placed on top of the gel coat. The form is covered with film and a mixture containing styrene is injected under vacuum, to distribute the styrene polymer in an equal layer throughout the form. When the polystyrene layer is hardened, the film is removed. The wing is being grinded, some additional items as flanges for gluing, and stabilising effects are being added to the upper and lower part of the wing. Finally the upper and lower parts are assembled, gluing the parts together with an extremely strong two component glue (including styrene). When the glue has reacted, some

additional casting is being done inside the wing. The wing is released from the form and it is ready for Hall II.

Hall II: After the wing has been released from the form, the edges of the wings are being cut and grinded to get a more smooth surface. In case some minor faults needs to be fixed these are done. Additional casting inside and outside the wing is done.

Hall III: In the end the wing is brought to Hall III, in which minor painting repairs, polishing and minor faults in general are fixed. Products for painting and filling contain styrene. The wing is send to the department for assembly to add the final mechanic parts and the production of the windmill wing is finalised.

Measurements

Strategy 1: 'The measured 8h-TWA' strategy

For a number of 39 workers selected randomly among workers in Hall I, Hall II and Hall III, personal daily measurements (8h TWA) concentration of exposure were carried out using passive (diffusive) samplers, applying a standard method for measuring the concentration of styrene in air (Brown *et al.*, 1981; Health and Safety Executive, 1985). Each person was equipped with 2 Perkin-Elmer Tubes, containing a Tenax polymer (Tenax TA), in the morning. Immediately after, the tube was opened and equipped with a diffusion cap. After exposure for 6-8 hours the tubes were collected and sealed. The tubes were stored in refrigerator during transport and storage before they were analysed. Samples were analysed using a Perkin-Elmer auto sampler GC-FID, equipped with a thermal desorber and a capillary column (Chrompack CP Sil 8 60m x 0.25 mm). Inlet and outlet split (100 ml/min and 10 ml/min). Oven temperature: 300°C. Trap: -30 - 300 °C. Limit of quantification (LOQ) of the method was approximately 0.1 µg/ml. Perkin-Elmer tubes with a normal sampling header were used. Pre experiments using passive sampling tubes equipped with back-up tubes had been used to investigate possible breakthrough. The samplers were placed on different people performing some of the highly exposed processes several times. Styrene was not found above the limit of detection on the back-up tubes. Following expression was used to calculate the concentration of airborne styrene during the sampling period for each of the exposed tubes:

$$\text{Concentration of styrene in air (mg m}^{-3}) = \frac{(m - m_{blank}) \times 1000}{U' \times t}$$

where m is weight (μg) of styrene on sample, m_{blank} is weight (μg) of styrene on blank (was equal to 0 for all samples), U' is the uptake rate $cm^3\ min^{-1}$ and t is the exposure time (min). The standard uptake rate of styrene for this kind of sampler is approximately 0.47 $cm^3\ min^{-1}$ according to (Health and Safety Executive, 1985).

As Tenax TA adsorbent from the passive samplers was desorbed by thermal desorption immediately before analysis by GC-FID, using a freezing trap connected to the gas chromatograph. No dilution of the styrene on the tube is involved in this type of desorption. The repeatability (day-to-day variation) of the method at low concentrations (1.7 μg) was found to be 6.6% (RSD) and 2.7% (RSD) at high concentrations (40.6 μg). It should be noted that tubes for validation were produced using manual injection, leading to a relatively high RSD. In case automatic injection was used, uncertainty would probably be reduced (<2%).

Strategy 2: The Logbook method (with PC measurements)

Processes performed during the day were identified and labelled according to the names used by the employees. 18 processes were identified in Hall I, 6 processes were identified in Hall II and 8 processes were identified in Hall III. Some of the processes had to be subdivided due to difference in exposure level depending on the place the worker was performing the process (up in form, inside form, at table etc.). Stay in cantina, visits at toilets etc. were included as a process ('Others elsewhere').

Logbooks (time measurements)

Workers were asked to fill in logbooks during the working day. It was made clear to all workers that the logbooks were confidential, to obtain the most reliable log keeping. The logbook period was three, separate weeks during a period of 6 months (the reference period). The workers kept log on when they start and stop each working process during the log period. Logbooks were collected in the end of each working day. In Figure 1, the design of the logbook for Hall I is shown.

Data on 979 logbooks (day measurements) of 367 persons were collected during the sampling periods.

NAME: SHIFT: Day O Night O DATE:

WORKING NO.:

		TIME									
PROCESS	Where?	*from*	*to*	*from*	*to*	*from*	*to*	*from*	*to*	*from*	*to*
Gelcoating	Outside form										
	In form										
Web 1.st layer											
Web											
Vacuum	Shooting										
	By form										
Stripping	Outside form										
	In form										
Flange of glueing	Outside form										
	In form										
	At table										
Lamination	Outside form										
	In form										
	At table										
Glueing	Inside form										
	Not inside										
Lamination	Inside form										
Others in Hall I											
Others elsewhere											

Figure 3. Design of the logbook used for time measurements in Hall I

Process concentration measurements

Personal measurements for estimating the process concentration (**PC**) were done during the period of data collection applying the method proposed by Nyeland et al. (Nyeland *et al.*, 2002a). Workers, performing the identified processes, were selected randomly. Number of measurements obtained for each process was 3 – 17 measurements. Processes with high levels of **PC** or performed large part of the day were preferred, when measurements were repeated.

Samples were collected using SKC pumps (10-50 ml/min or 50-200 ml/min) calibrated separately, on SKC 150 mg Silica gel Tubes (226-10, lot. no. 1838) or SKC 30 mg Tenax Tubes (226-35, lot. no. 1290). All samplings were done in duplicates with the tubes mounted in the breathing zone, 1 cm apart. The position of the tubes (workers left or right hand side) was recorded. Sampling period was 10-25 minutes. The NIOSH 1501 method was applied (NIOSH, 1994). *N,N*-Dimethylformamide (>99%, Merck) was used as desorption liquid, silica gel tubes were used for short-term sampling (<15 min) and Tenax tubes were used for longer short-term sampling (15-25 min), for exposure measurements at higher concentration levels of styrene. Decisions were done according to previous observations (Nyeland *et al.*, 2002a).

Samples were stored in a transportable refrigerator, brought to the laboratory and stored at 5°C. The A- and B-layers (main- and control layer) from each tube were desorbed separately in 1 ml *N,N*-dimethylformamide for 24 hours before solutions were analysed on a Perkin-Elmer FID-GC equipped with a capillary column (Chrompack, WCOT Fused Silica (CP-Sil 8 CB), CP7452, 25 m x 0.25 mm). Temp. 70 - 110°C; 110 - 180°C. Injection volume: 1,0 µL.

A Perkin-Elmer Auto system XL gas chromatograph (GC), equipped with a FID was used to determine the content of styrene in all analysis performed. LOQ for the liquid desorption method was approximately 0.1 mg/ml.

Strategy 3: Logbook method (with 8h TWA measurements)

Measurements for Strategy 3 were:

- Passive samplings (8h TWA measurements) as collected in Strategy 1
- Logbooks as collected in Strategy 2

used to estimate **PC**s.

Correlating active- and passive sampling

It was decided to use passive sampling when sampling daily exposure due to risk for breakthrough of tubes, when sampling using pumps (active sampling). To calibrate the use of passive sampling to the active sampling, 12 daily measurements (i.e. 12 workers), covering the area of concentration levels. All measurements were done in doublets 1 cm apart. To avoid breakthrough on the active sampled tubes, a low rate of pump flow was chosen (20 ml min^{-1}) and tubes for the active sampling were changed every 30 minutes. The daily measurements of the active and passive samples have been compared using orthogonal regression corresponding to a so-called functional model relating the measurements (Fuller, 1987). As the relative measurement error was believed to be constant over the range of measurement values, an orthogonal regression on the logarithmic values was used.

Background measurements

Active measurements using SKC-pumps and silica gel tubes were done as well as measurements performed by a direct reading instrument – a Photo Ionisation Air Monitor (PIAM) (PE Photovac, model 2020). This was done for 10 days measurements, at different concentration levels, to span the area for calibration of the signal from the PIAM to the active measurements. Further background measurements were done using the PIAM.

Observations showed that no constant background level existed in Hall I, in general background level in the hall was highly depending on processes performed at each form. **PC** of the process 'Others in Hall I' was assigned to be equal to the value of **PC** for process 'Web' (not including 'Web, 1st layer'). It was decided to use **PC** of the process 'Web' as **PC** for the process 'Others, Hall I' because no products containing styrene was used during the process 'Web'. In Hall III it was decided to use **PC** of the process 'Polish' as **PC** for the process 'Other, Hall III' because no products containing styrene was used during the process 'Polish'.

Data handling

A flow sheet of the data collected is shown in Figure 4 below.

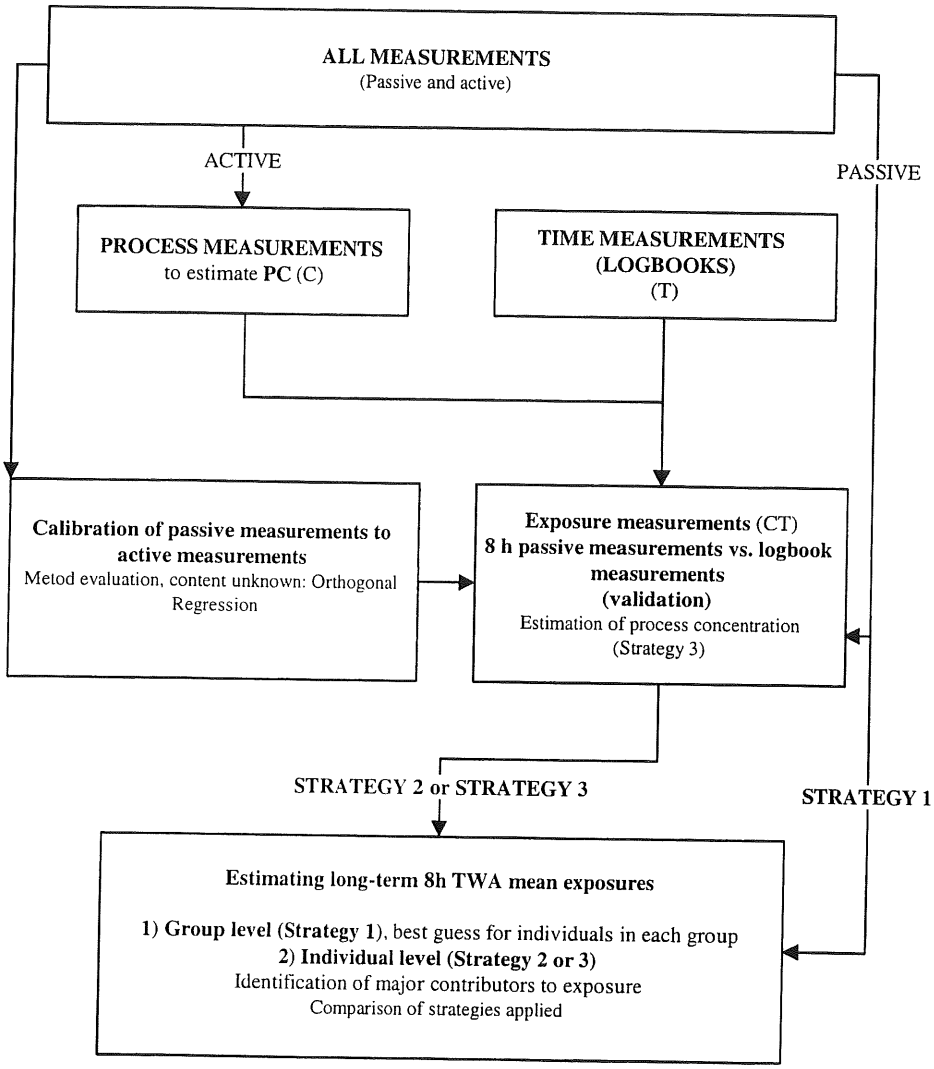


Figure 4. Flow sheet of data collected and data handling in connection with data analysis

8h TWA exposure concentrations at the individual level were estimated using the logbook method, by obtaining the TWA-matrix described above. The TWA matrix is derived from a matrix of fractions of time the worker spent performing a given process during a working day, and a vector containing values of process concentrations of all processes at the factory. This matrix can be

transformed to the *JP*-matrix, containing information on dose received by workers per logbook day (Olsen, 1994) by multiplying a vector containing the total working time for each day. The *JP*-matrix is central for further analysis of individual exposures.

Process concentrations (**PC**) were measured in duplicate. In case the RSD (relative standard deviation) was greater than 25% the value was set equal to the largest value of the two. It is supposed that the greatest exposure measured must be the most reliable. In some cases extreme values were observed. Aerosols of styrene can be formed when some of the processes are carried out. During sampling these droplets can deposit inside the measurement tubes. Such observations were rejected as outliers. When estimating **PC**, Grubbs test for outliers was used as test for outliers as proposed in ISO 5725-2 (International standard ISO 5725-2, 1994).

RESULTS

Strategy 1

Figure 5 shows the 8h TWA repeated measurements obtained in Hall I, Hall II and Hall III sorted by worker. A total number of 110 measurements were achieved.

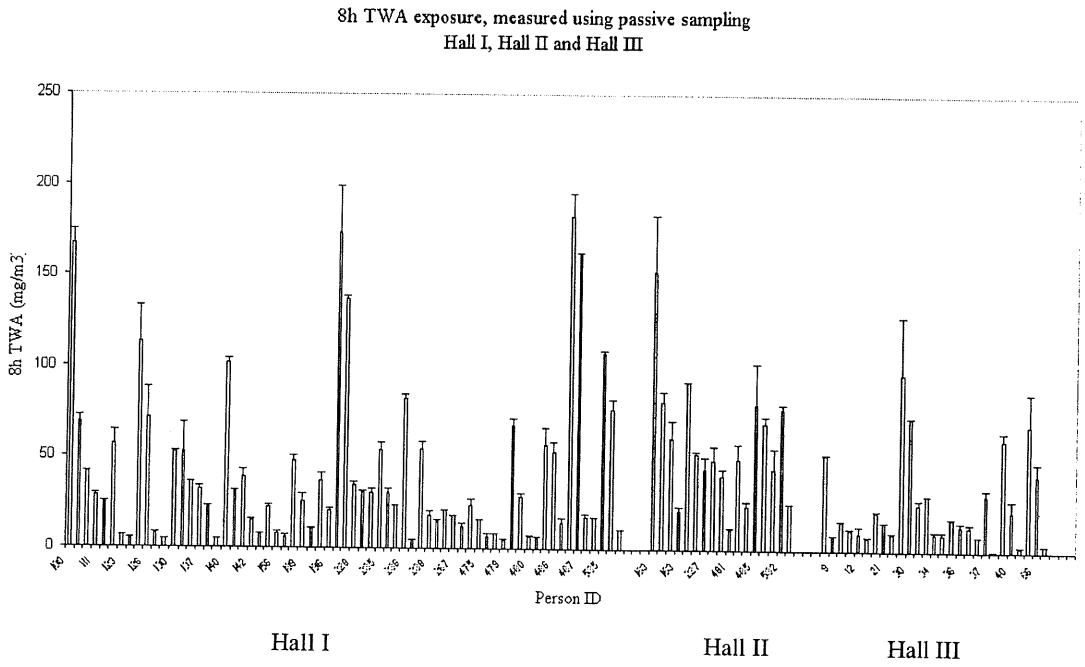


Figure 5. 8h TWA , repeated measurements using passive sampling. All measurements obtained during week 2 and 3 are shown, sorted by department and person. SDs of each measurement is shown (measurements were carried out in duplicates).

To describe the measured exposure in the factory and to estimate a mean value of the exposure in each of the departments, taking into account the between- and within worker variability, a mixed model is used:

MODEL: $Y_{h(ij)} = ln(X_{h(ij)}) = \mu_y + \alpha_h + \beta_{h(i)} + \varepsilon_{h(ij)}$

$X_{h(ij)}$	-	Exposure level on the j-th day for the i-th worker in the h-th department
μ_y	-	The underlying, mean exposure level over all jobs
α_h	-	The fixed effect of the h-th department
$\beta_{h(i)}$	-	The random effect of the i-th worker (~iid; $N(0,\sigma^2_{B,h})$)
$\varepsilon_{h(ij)}$	-	The random effect of the j-th day for the i-th worker (~iid; $N(0,\sigma^2_{W,h})$)

Departments are used as a fixed effects. It is assumed that data are lognormal distributed and thus the analysis is performed on the log transformed data.

Data on 39 workers were analysed using PROC MIXED, (SAS statistical software, (Littell *et al.*, 1996)). The SAS-statement was:

```
PROC MIXED data=mixed_ny maxiter=100 method=REML;
class depmt;
model logC_pass=depmt;
random persid;
lsmeans depmt;
run;
```

Output is shown in Table 3 below. Estimates for the GM for the three departments and between- and within worker variabilities (σ_B^2 and σ_W^2) are shown.

Table 3. Strategy 1 applied. Estimating mean exposure level in Hall I, Hall II and Hall III at population level

Strategy applied	Department	GM [mg m^{-3}]	σ_B^2	σ_W^2
Strategy 1	Hall I:	26.5	~ 1	3.0960
	Hall II:	73.3	~ 1	1.4428
	Hall III:	15.9	~ 1	3.2008

GM: Geometric mean, σ_B^2 : Between worker GSD, σ_W^2 : Within worker GSD

It seems as if all of the departments fulfil the criteria stated by Rappaport (Rappaport, 1991) as being HEGs, for which 95% of the individual arithmetic mean concentrations (between workers) are within a factor of 2 ($GSD^{3.92} < 2$). Variability within workers in all groups are large, and thus between worker variabilities are found to be very small or not possible to estimate. Distributions of exposure of the populations in each of the halls are shown in Figure 6.

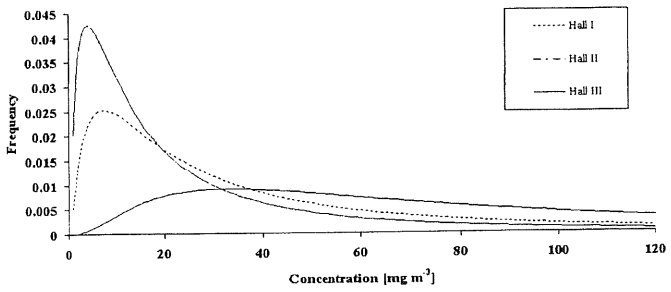


Figure 6. Estimated exposure distributions of workers' AMs exposures in Hall I, Hall II and Hall III.

The best estimate applying Strategy 1 for an arithmetic mean exposure of an individual worker from the population shown in Figure 6, is the GMs, estimated for the whole population in each of the departments.

Strategy 2: The Logbook method (PC measured)

Process concentrations

Process concentration measurements were found to be normally distributed, which was tested by using a Kolmogorov-Smirnov normality test ($p>0.15$), using the statistical software MINITAB version 13. These short-term levels of **PC**s are shown in Figure 7. Name of the processes and in which department they take place, are shown in Table 4 together with the measurements carried out to obtain the estimated **PC**. One of the processes 'Gluing, inside', Hall I, differs from the rest of the processes in which the **PC** was much higher compared to the others.

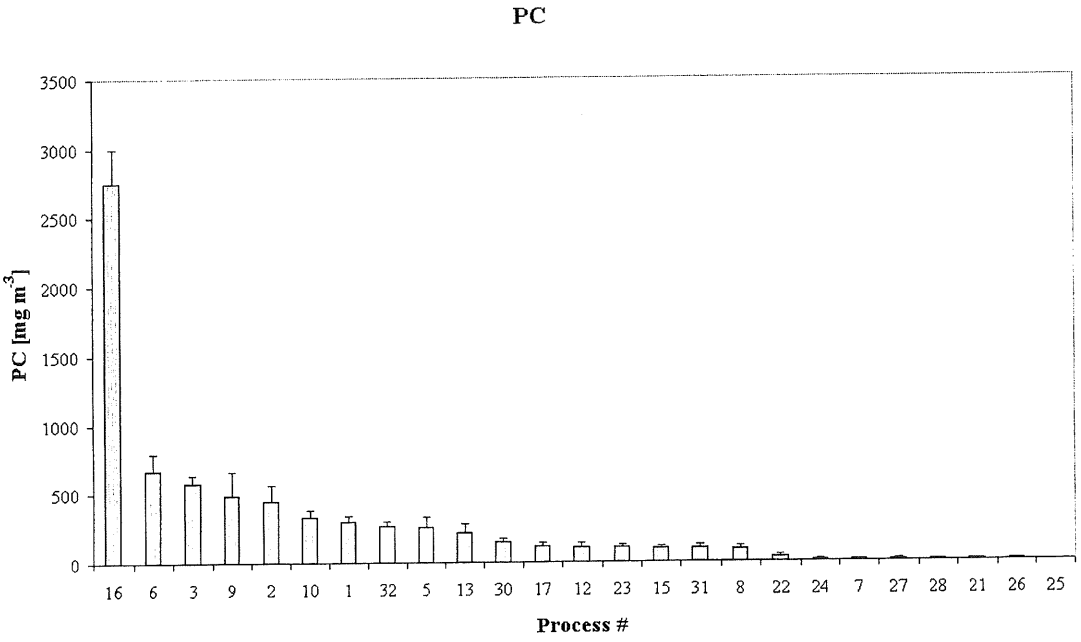


Figure 7. Estimated Process concentrations (measured) of all processes, standard deviations are shown. Sorted in descending order.

Table 4. Names and id number of processes in Figure 7.

Proc id #	Name of process	Department (Hall)	PPE (Yes/No)	Number of measurements obtained to estimate **PC**	**PC** [mg m^{-3}]	SD	RSD	**PC**/OEL
1	Stripping, in form	I	Yes	12	294,18	41,863	14,231	2,78
2	Stripping, outside form	I	Yes	7	447,68	114,16	25,501	4,22
3	Casting, inside	I	Yes	9	574,48	58,049	10,105	5,42
5	Gelcoating, in form	I	Yes	8	254,73	74,247	29,148	2,40
6	Gelcosting, outside form	I	Yes	9	666,89	124,46	18,662	6,29
7	Web	I	No	4	10,217	3,5387	34,635	0,10
8	Web, 1st layer	I	Yes	7	91,804	26,308	28,657	0,87
9	Lamination, inside	II	Yes	4	486,65	171,13	35,164	4,59
10	Lamination, outside form, Hall II	II	Yes	5	328,16	53,936	16,436	3,10
12	Flange of gluing, in form	I	Yes	3	109,67	28,428	25,922	1,03
13	Flange of gluing, outside form	I	Yes	7	216,18	64,786	29,969	2,04
15	Gluing, in form	I	Yes	7	95,58	15,787	16,517	0,90
16	Gluing, inside	I	Yes	12	2747,2	251,04	9,1383	25,9
17	Painting	III	Yes	14	117,04	21,704	18,544	1,10
21	Polishing	III	Yes	3	7,5376	2,2374	29,683	0,71
22	Grinding	I/II	Yes	7	36,625	8,686	23,716	0,35
23	Filling	III	Yes	8	104,83	15,329	14,623	0,99
24	Vacuum	I	No	6	12,221	3,3734	27,604	0,12
25	Other elsewhere	I/II/III	No	-	0			-
26	Other, Hall III	III	No	3	7,5376	2,2374	29,683	0,71
27	Other, Hall I	II	No	4	10,217	3,5387	34,635	0,10
28	Other, Hall II	I	No	4	8,899	3,3421	37,556	0,08
30	Lamination, in form	I	Yes	9	149,83	23,241	15,511	1,41
31	Lamination, outside form, Hall I	I	Yes	7	95,346	27,453	28,794	0,90
32	Lamination, at table (aggr.)	I/II	Yes	17	264,6	31,632	11,955	2,50
	Total number of measurements obtained:			176				

PPE – Personal Protective Equipment

As the process 'Lamination, at table' was found to be similar in Hall I and Hall II these processes were aggregated to one estimated **PC**. Similar observation was done for the process 'Grinding'. Uncertainty in estimating **PC**, have been mapped in details using an uncertainty budget (Nyeland *et al.*, 2002a). The process 'Stripping, in form' was used for illustration.

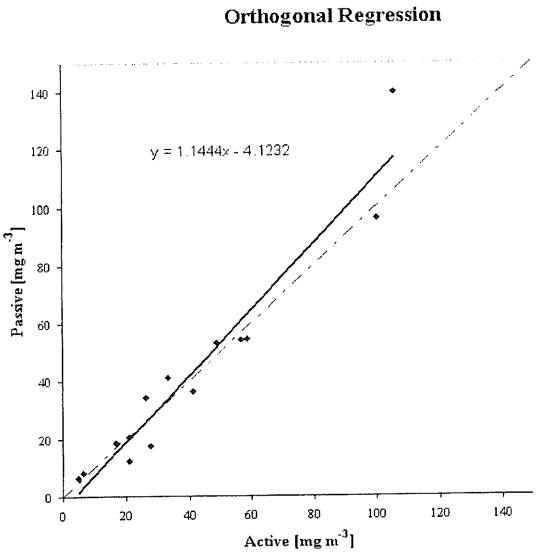
Logbooks

All of the 967 logbooks were entered in a database to estimate 8h TWAs. From the logbooks the time resolution of the time registrations in the logbooks in Hall I and Hall III was 5 minutes for each process. According to the logbooks the time registration was much more rough in Hall II, resolution 15 or 30 minutes.

Validation of exposure estimates obtained applying the logbook method

Correlating active- and passive sampling (Functional model)

Due to the fact that both x and y were subject to uncertainty, an orthogonal regression (functional model, errors in variables) was performed to assess the relation between content in active- and passive samples. The orthogonal regression on the log transformed data showed a good agreement between the two methods with no need for further calibration between the methods (Figure 8.1 and 8.2).



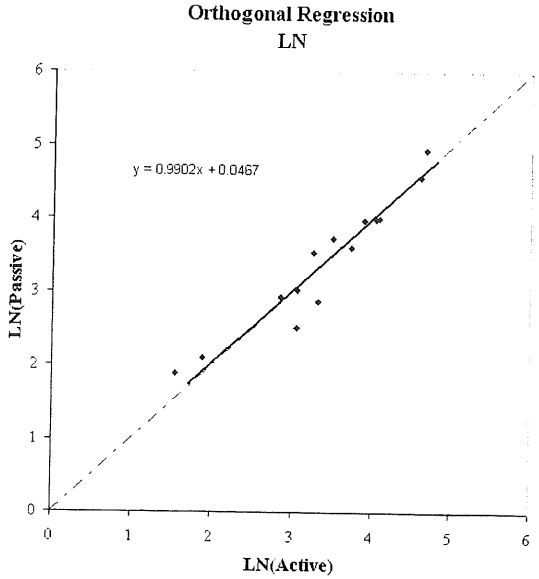


Figure 8.1 and 8.2. Figure 8.1 shows correlation of active and passive sampling using orthogonal regression (functional model). Figure 8.2 shows the correlation for the log transformed data.

Correlating 8h TWA logbook measurements and measured 8h TWA

To validate the estimated exposures applying logbook method, values of measured 8h TWAs and 8h TWA measurements obtained applying the logbook method, was correlated. Measurements obtained in Hall I, did correlate well (Figure 9). It is of note that data are not log transformed.

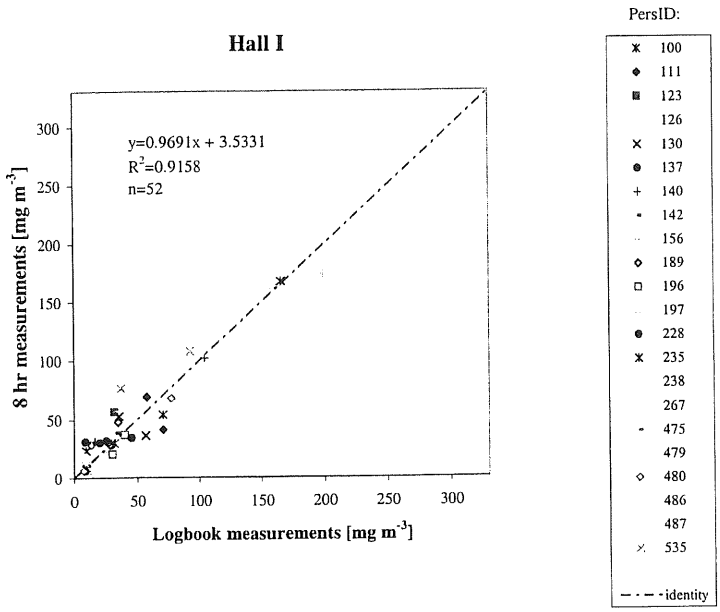


Figure 9. Hall I. Correlation of 8h TWA measurements and logbook measurements, (applying Strategy 2). Single day measurements.

A few outliers had to be eliminated (Table 5), due to gross error as a result of either styrene aerosols on tubes during sampling or improperly log keeping.

Table 5. Outliers eliminated before correlation of passive sampling measurements and logbook measurements

Tube no.	PersID	Department	Reason	Processes
P60/P61	266	Hall III	Dirty header, tubes dropped on floor During lamination, inside	Incl. lamination
P192/P193	475	Hall I	Dropped on floor during gluing	Incl. gluing
P246/P247	266	Hall III	Dirty header	Incl. lamination
P66/P67	197	Hall I	Dirty header	Incl. gel coat
P220/P221	197	Hall I	Dirty header	Incl. gel coat
P173/P174	475	Hall I	Improperly logbook registration	-
P264/P265	475	Hall I	Improperly logbook registration	-

Tube no. – number of tube pairs from passive sampling; PersID – number to identify workers

Measurements obtained in Hall II did not correlate. During data collection unfortunately it had not been possible to motivate workers to fill in the logbooks in a proper manner. Time recordings obtained were thus too incorrect for any proper use.

In Hall III (Figure 10) correlation was not as good as in Hall I. Exposure estimates obtained applying Strategy 2, seemed to be a little overestimated. According to the logbooks the majority of workers in Hall III did record time for each process including time spent on preparations, time intervals ought to be recorded as 'Others in Hall III'.

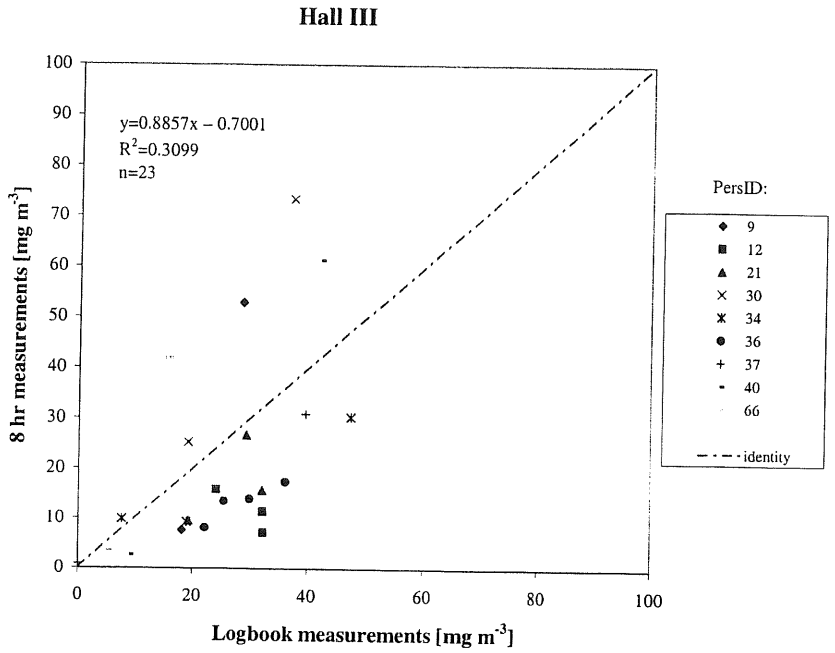


Figure 10. Hall III. Correlation of 8h TWA measurements and logbook measurements, (applying Strategy 2). Single day measurements.

Strategy 3: The Logbook method (8h TWAs). Estimating process concentrations using (PROC GLM)

Hall I

To estimate the **PC**'s from 8h TWA day measurements and the logbook-matrix, the first step was to check whether the 'design' of the logbook-matrix was suitable for estimating the coefficients (that the columns were linearly independent). Daily exposures estimated from the logbooks and process concentrations were used as the aggregated daily measurements (y-values in the matrix). Figure 11 verifies that the design of the logbook-matrix is suitable for estimating the coefficients (**PC**s).

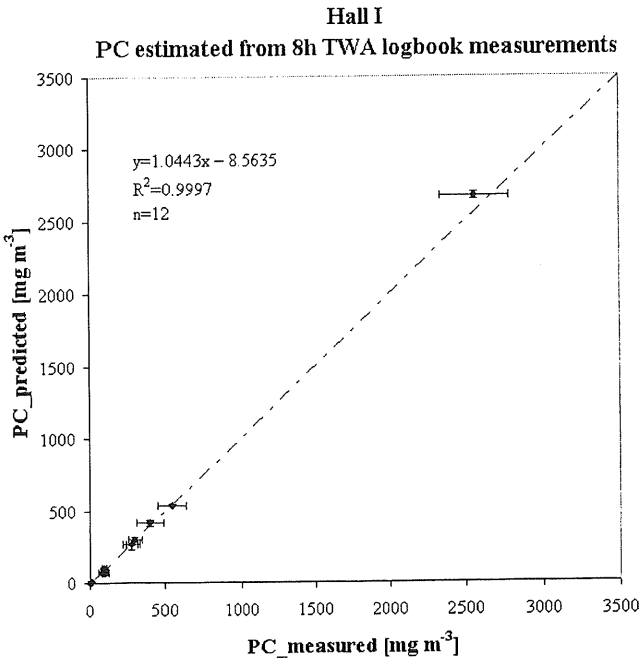


Figure 11. Hall I. Correlation of **PC**s estimated from Logbook measurements and **PC**s measured. Standard deviations are shown.

Subsequently **PC**s were estimated from logbooks and 8h TWA solving the TWAC-matrix using PROC GLM (SAS statistical software).

SAS-statements:

```
proc glm data=hallI;
model c_8hTWA= proc1 proc2 proc6 proc7 proc8 proc12 proc13 proc15 proc16 proc24
proc25 proc27 / int;
run;

proc glm data=hallIII;
model c_8hTWA= proc17 proc21 proc23 proc25 proc26 / int;
run;
```

An initial analysis showed that the time spent at the two processes 'Web 1.st layer' and 'Web' in Hall I was linearly dependent. These processes were lumped before data was analysed. In Figure 12 correlation of estimated **PC**s and measured **PC**s is shown.

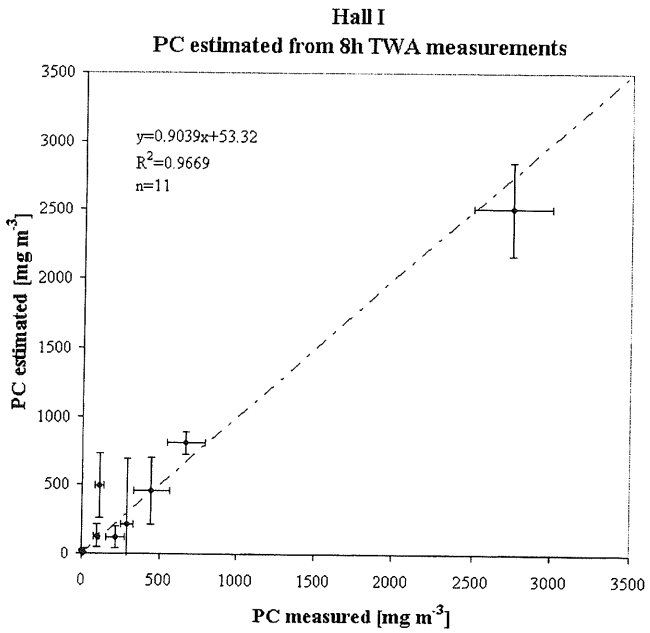


Figure 12. Hall I. Correlation of **PC**s estimated from passive sampling measurements and **PC**s measured directly from process. Standard deviations are shown.

Finally individual 8h TWAs of the workers in Hall I, estimated applying Strategy 2 and Strategy 3 compared to measured 8h TWAs values, are shown in Figure 13. Estimates obtained applying Strategy 2 seems to be closer to the measured values compared to estimates obtained applying Strategy 3.

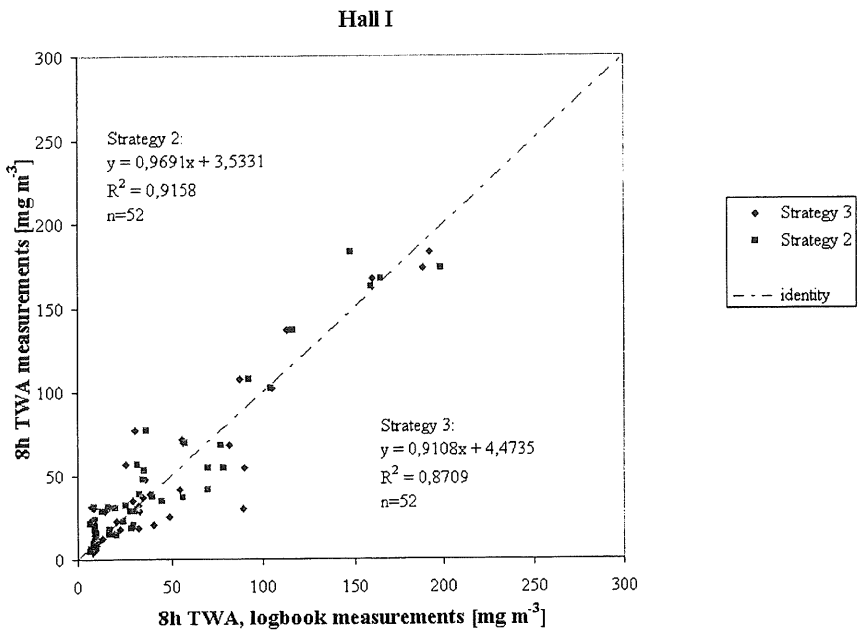


Figure 13. Hall I. Correlation of 8h TWA measurements and logbook measurements (applying Strategy 2 and Strategy 3). Single day measurements.

Hall II

It was not possible to obtain reliable estimates for **PC**s on data obtained in Hall II.

Hall III

Estimates for **PC**s in Hall III could be obtained, but they were associated with much larger uncertainties compared to estimates in Hall I.

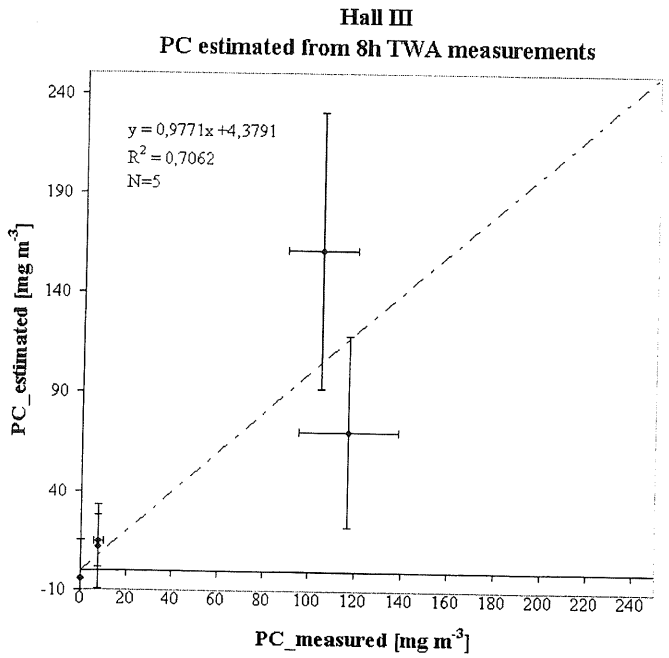


Figure 14. Hall III. Correlation of **PC**s estimated from passive sampling measurements and **PC**s measured directly from process. ± Standard deviations are shown.

As **PC** for the process 'Other elsewhere' was estimated to be negative (about –5) it was assigned to be 0 in subsequent calculations.

Finally individual 8h TWAs of the workers in Hall III, estimated applying Strategy 2 and Strategy 3 compared to measured 8h TWAs values, are shown in Figure 15. Estimates obtained in Hall III applying Strategy 3 seems to be closer to the measured values compared to estimates obtained applying Strategy 2 on the contrary to what was observed in Hall I (Figure 13).

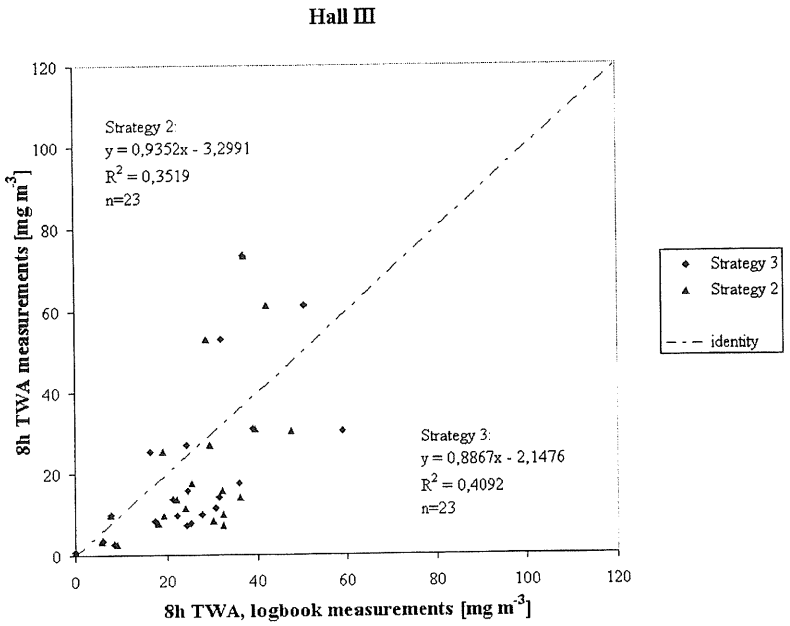


Figure 15. Hall III. Correlation of 8h TWA measurements and logbook measurements (applying Strategy 2 and Strategy 3). Single day measurements.

Estimating individual mean 8h TWAs

The validation of logbook methods (Figure 9) shows that it is possible to estimate 8h TWA applying Strategy 2 or Strategy 3. Logbooks had been distributed to all of the workers in the three departments during the logbook period, which was 3 separate weeks during a reference period of 6 months. Individual 8h TWAs during the logbook period were obtained applying Strategy 2 on data obtained for persons in Hall I. Strategy 3 was applied to obtain 8h TWAs for persons in Hall III because better estimates of 8hTWA were obtained (estimates are closer to the line of identity, Figure 15). 840 estimated 8h TWAs exposures were obtained for 328 workers (2-8 repeated measurements of each worker). This large amount of data was collected during a period of effectively 12 working days. Individual arithmetic means of 8h TWA during the log period were calculated, shown in Figure 16a, 16b and 17.

Figure 16a

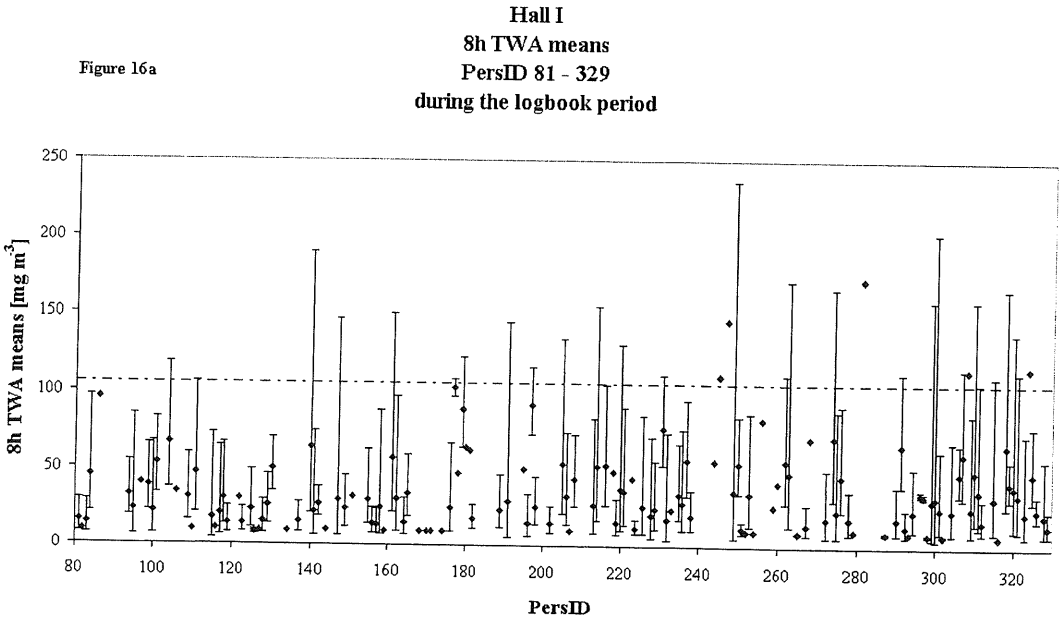


Figure 16b

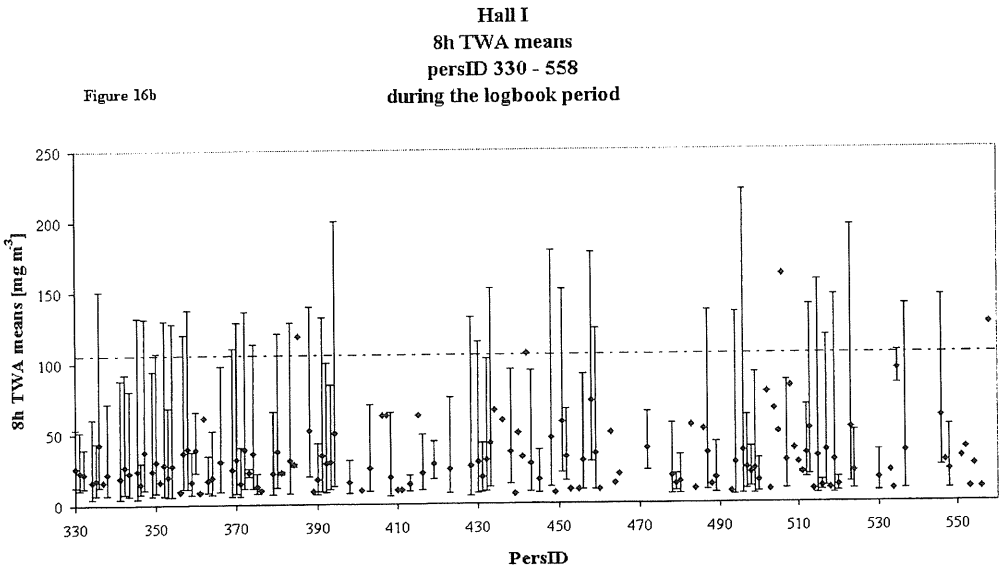


Figure 16a and 16b. Hall I. Arithmetic mean values of 8hTWA exposures for individual workers during the log period. Log transformed standard deviations are shown as well as OEL of styrene.

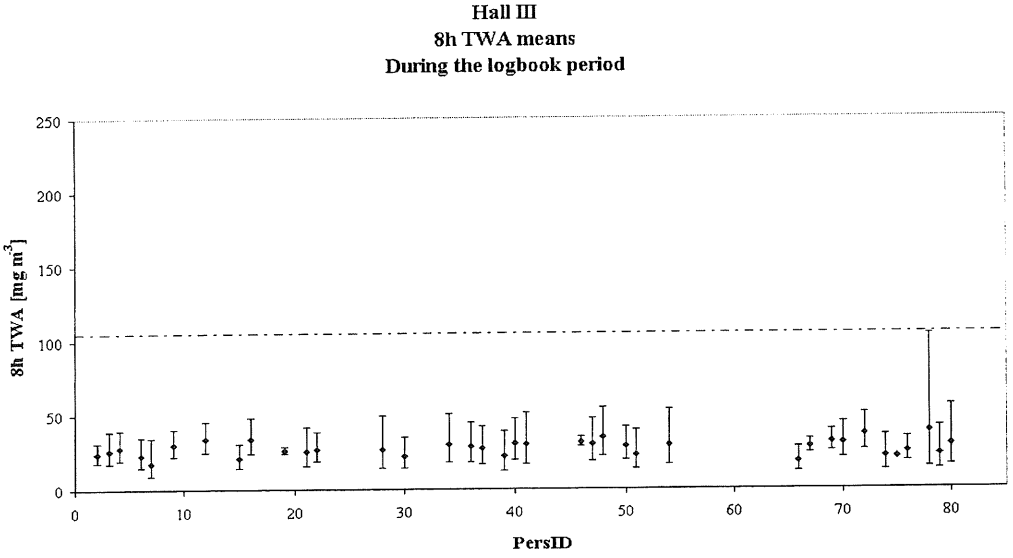


Figure 17. Hall III. Arithmetic mean values of 8hTWA exposures for individual workers during the log period. Log transformed standard deviations are shown as well as OEL of styrene.

It seems as if exposure during the log period varies more in Hall I than in Hall III. Exposure level is higher in Hall I and OEL is more often exceeded by individual workers in this department.

Identifying major exposure sources

Data provided contains quantitative information for risk management, which can be used for decisions on intervention at the individual level. Major exposure sources can be identified. Table 6 shows all processes in Hall I, and Hall III ranked according to short-term exposure (**PC**) and long-term exposure (mean available daily dose for a worker during the log period). Short-term exposure concentration is relevant when considering exposure to irritants. Long-term exposure dose is relevant when considering exposure to carcinogens.

Table 6. Processes ranked according to short-term exposure and according to long-term daily available dose per worker in Hall I and Hall III.

Hall I

Short-term exposure					Long-term exposure			
Rank #	Proc id #	Name of process	**PC** measured [mg m^{-3}]	SD [mg m^{-3}]	Proc id #	Name of process	Mean available daily dose [mg min m^{-3}]	SD [mg min m^{-3}]
1	16	Gluing, inside	2747,2	251,0	6	Gelcoating, outside form	4172,5	371,9
2	6	Gelcoating, outside form	666,9	124,5	16	Gluing, inside	3521,4	409,0
3	3	Casting, inside	574,5	58,0	27	Other, in Hall I	2561,9	71,7
4	2	Stripping, outside form	447,7	114,2	15	Gluing, in form	2127,2	211,4
5	10	Lamination, outside form	328,2	53,9	7	Web	1980,9	74,3
6	1	Stripping, in form	294,2	41,9	13	Flange of gluing, outside form	1833,8	186,8
7	32	Lamination, at table aggregated	264,6	31,6	30	Lamination, in form aggregated	1672,9	185,9
8	5	Gelcoating, in form	254,7	74,2	2	Stripping, outside form	1608,2	174,6
9	13	Flange of gluing, outside form	216,2	64,8	5	Gelcoating, in form	1164	193,7
10	30	Lamination, in form aggregated	149,8	23,2	1	Stripping, in form	912,1	112,7
11	12	Flange of gluing, in form	109,7	28,4	24	Vacuum	648,9	37,2
12	15	Gluing, in form	95,6	15,8	3	Casting, inside	524,8	101,6
13	31	Lamination, outside form aggregated	95,3	27,5	32	Lamination, at table aggregated	334,4	89,3
14	22	Grinding	36,6	8,7	31	Lamination, outside form aggregated	258,5	50,4
15	24	Vacuum	12,2	3,4	12	Flange of gluing, in form	232,1	51,8
16	7	Web	10,2	3,5	10	Lamination, outside form	108,2	108,2
17	27	Other, in Hall I	10,2	3,5	22	Grinding	27,1	16,2
18	25	Other elsewhere	0	-	25	Other elsewhere	0	-

Table 6 (continued)

Hall III

Short-term exposure					Long-term exposure			
Rank #	Proc id #	Name of process	**PC** measured [mg m^{-3}]	SD [mg m^{-3}]	Proc id #	Name of process	Mean available daily dose [mg min m^{-3}]	SD [mg min m^{-3}]
1	17	Painting	117,0	21,7	23	Filling	4811,2	409,9
2	23	Filling	104,8	15,3	17	Painting	4729,5	240,0
3	21	Polishing	7,5	2,2	21	Polishing	2547,0	78,8
4	26	Other, in Hall III	7,5	2,2	26	Other, in Hall III	1303,2	106,8
5	25	Other elsewhere	0	-	25	Other elsewhere	0	-

Decisions can be done on where to intervene at the individual level, based on data obtained e.g. whether time spent at a process should be changed or emission from a process should be reduced. The process contributing most to the long-term mean daily dose seems to be the process 'Gelcoating, outside form' compared to the short-term exposure for which it is the process 'Gluing, inside'. When decisions on where to intervene to lower exposure it should be preferred to lower exposure from the process 'Gelcoating, outside form' either by enhancing the LEV or by reducing time spent at the process. It seems as if the process 'Gluing, inside' is the second highest contributor to the available daily dose. As the process only takes about 20 minutes, some kind of intervention by exhaustion should be done inside the windmill wing to reduce the exposure level.

It is remarkable that 'Other, in Hall I' is ranked as the third largest contributor to the available daily dose, especially due to the fact that workers do not ware any personal protection performing this 'process'. Focus should thus be turned to the general ventilation in this department, to lower exposure during preparations.

In Hall III it seems as if it is the process 'Filling', which contributes most to the available daily dose.

To bring exposure under control at the individual level (Nyeland *et al.*, 2002b) the next step is to identify which persons are exposed to higher levels and to trace the causes which contribute the most to the elevated exposures. Intervention is done at the specific individual level followed by exposure assessment to check whether intervention has been successful. Otherwise intervention and exposure assessment are redone until exposure is brought under control and worker is ready for population monitoring (Holst *et al.*, 2002; Nyeland *et al.*, 2002b).

Comparing the strategies applied

Uncertainty due to measurement procedure when estimating a workers 8h TWA **a single day**, is expected to be larger applying the logbook methods. Uncertainty in estimating **PC** of each process performed and uncertainty in the time recordings during the day contribute to the total uncertainty on estimating the 8h TWA of a single day.

Applying Strategy 1 uncertainty in measuring 8hTWA of a single day is the only uncertainty due to sampling, transport, storage and analysis.

Table 7. Uncertainty sources in measurement procedures of the three strategies for obtaining an 8h TWA measurement on a worker **a single day** for a worker

Strategy	Measurement	Sources of uncertainty	RSD (%) of 8h TWA	Ref.
Strategy 1	8h TWA	Sampling, Transport, Storage, Analysis	8.4	Calculated
Strategy 2	**PC** + logbook	Day to day variation (within-, between-worker, emission from process), Sampling, Transport, Storage, Desorption, Analysis Time recordings	34.3	Calculated
Strategy 3	8h TWA + logbooks → estimated **PC** + logbook	Sampling, Transport, Storage, Analysis Time recordings	35.2	Calculated

Table 7 shows that applying Strategy 1 an 8h TWA measurement of a worker **a single day**, is associated with a smaller uncertainty, compared to a 8h TWA a single day, applying the logbook methods. When thermal desorption is applied, compared to **PC** measurements (liquid desorption), measurements uncertainty is supposed to be small.

Applying the logbook methods individual exposure estimates of many days are obtained.

When estimating **arithmetic mean** 8h TWA exposure, uncertainty of estimates for a single worker's exposure is reduced compared to the uncertainty associated with the mean 8h TWA value of workers exposure obtained applying Strategy 1, in which the best guess for an individual workers exposure is the estimated GM of the population exposure. As it is the long-term arithmetic mean air exposure concentration, which is the measure to be related to risk of adverse health effects due to chronic exposure for a single worker (Rappaport, 1991), it is desirable to estimate individual exposures connected with the lowest possible uncertainty.

In Figure 16a, 16b and 17 mean values of 8h TWA individual exposure estimates of all workers during the log period in Hall I and Hall III, applying Strategy 2 are shown. Compared to the estimates obtained applying Strategy 1, when applying Strategy 2, estimates are associated with a much smaller uncertainty. Even though the uncertainty in estimating 8h TWA of **a single day** is found to be smaller under Strategy 1 (higher degree of precision), benefits are much larger under Strategy 2 or 3, when estimating the long-term **arithmetic** 8h TWA **mean** exposure of an individual worker, because exposure data for a large number of days are obtained (higher degree of accuracy).

All three strategies provide answers to the question: are workers in general too high exposed?
In addition, Strategy 2 and Strategy 3 answer the question: which processes contribute the most to workers dose? Information for decisions on i.e. where to intervene most effectively is, therefore, provided, applying Strategy 2 or Strategy 3. In case the purpose of the exposure assessment is to bring exposure under control, Strategy 2 and Strategy 3 are useful because they identify and quantify specific where to intervene. Highly emitting processes or their surroundings can be changed or time spent at specific processes can be reduced to reduce exposure and bring individual exposures under control.

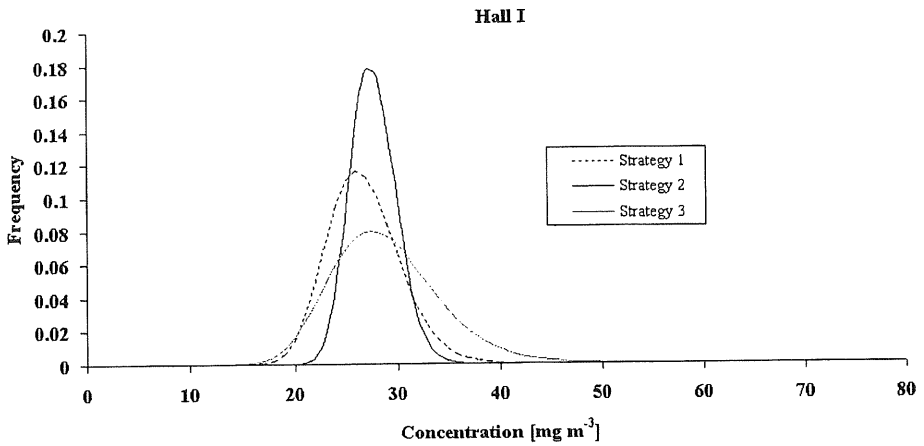
Comparing exposure estimates obtained at the population level applying each of the strategies

To compare exposure estimates obtained under Strategy 1, 2 and 3 respectively, data obtained under each strategy for the 39 workers described above, were analysed at the population level, as a mixed model. Estimates for each of the departments were obtained (Table 8 and Figure 18). As data for Hall II, under Strategy 2 and Strategy 3 previously had shown to be insufficient, only data from Hall I and Hall III were compared.

Table 8. Population level. Estimated GM values of exposure to styrene and the associated uncertainties depending on the sampling strategy applied. At the population level.

Strategy applied	Hall	GM [mg m^{-3}]	GSD
Strategy 1	I:	26.5	1.1392
	III:	15.9	1.2143
Strategy 2	I:	27.1	1.1000
	III:	26.8	1.0800
Strategy 3	I:	28.2	1.1959
	III:	23.3	1.1564

GM: Geometric mean, GSD: Geometric standard deviation. Parameters most commonly used to describe lognormal distributions. GSD corresponds the estimated standard error from PROC MIXED.



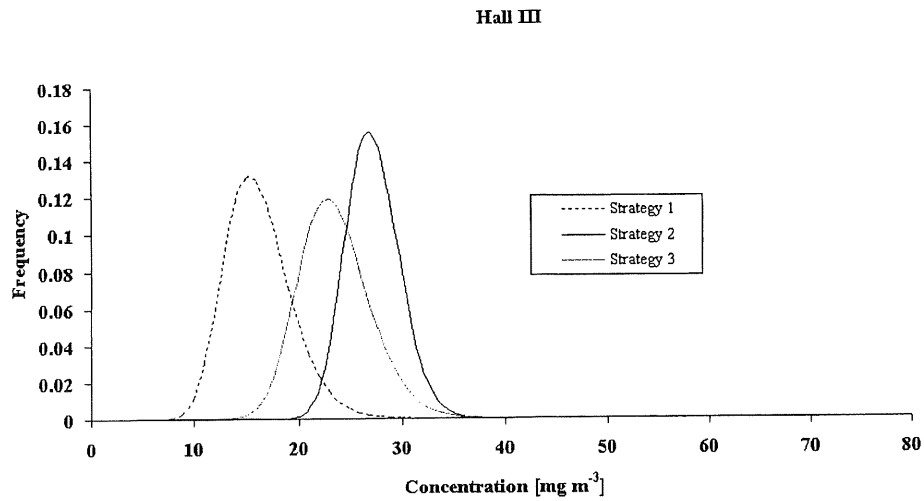


Figure 18. Distributions showing the uncertainties in estimating exposures of the populations in the two departments Hall I and Hall III, obtained applying different sampling strategies

Figure 18 shows that applying Strategy 1, 2 and 3 for Hall I, all most identical estimates are obtained in each of the departments. Strategy 2 estimates the mean population exposure associated with the smallest uncertainty, which should be expected because these estimates are based upon a larger number of days. Strategy 1 and Strategy 3 seem to be associated with larger uncertainties. Data obtained for Hall III, seems to be biased towards higher values applying Strategy 2 or 3. This is in accordance with what was observed previously (Figure 10). The associated uncertainties seem to be all most equal applying any of the strategies.

DISCUSSION

Estimating the long-term arithmetic mean air exposure concentration is the central task for exposure assessments, because this measure of exposure can be related to risk of adverse health effects due to chronic exposure for a single worker (Rappaport, 1991). This goal is fulfilled by all of the three unbiased strategies applied in the present paper, but the techniques to obtain the goal differs as do the associated uncertainties of the estimates and the usefulness of data.

During the last decade Strategy 1 has become the most commonly applied measurement strategy to obtain unbiased data for exposure assessments. Applying this strategy a large number of data are needed to develop meaningful and informative empirical models (Kromhout, 2002). In 1994 another approach, the logbook method (Strategy 2), to obtain unbiased data for exposure assessment was proposed (Olsen, 1994). An extended version of the logbook method, Strategy 3, is applied in this paper. Traditionally new methods are validated against well known, well tested methods. In this paper the new measurement strategy (Strategy 3) is thus validated, tested and compared with the measurement strategies Strategy 1 and Strategy 2. In the present study all three strategies are applied to obtain a unique dataset to be used for comparison of the strategies and their usefulness.

Applying Strategy 1, only two measurements pr. worker are needed for estimating average σ_W^2 or σ_B^2 in the exposure model. Compared to this, the logbook methods provide larger number of exposure measurements pr. worker (number of days in the logbook period e.g. in a three weeks). A better estimate of the arithmetic mean exposure of the individual worker is obtained under Strategy 2 although the uncertainty in estimating exposure of a single day is larger than under Strategy1. This is in agreement with the observations in the present paper, in which uncertainty on the logbook estimates of general exposures in the three departments is reduced compared to the uncertainty on the estimates obtained, under Strategy 1. Under Strategy 1, the object of measurement is the exposure of a population of workers and the measurand is the population distribution of individual arithmetic mean exposures. Thus random errors will be larger. This kind of sampling strategy can be applied at workplaces at which it is possible to divide workers in proper HEGs fulfilling the criteria defined by Rappaport (Rappaport, 1991). The way work is organised at the workplace needs to be appropriate for dividing workers in HEGs, to obtain proper exposure estimates. In the present paper, all of the three departments fulfil the criteria. Exposure information obtained for a HEG of workers, can be used for intervention at the general level.

In the present paper the logbook methods could not be applied in Hall II. Workers in Hall II were low motivated and the resulting logbook registration was useless. In Hall III time registration by workers in general were more rough compared to the log keeping in Hall I. Time registrations for each process were in general too long compared to the actual time spent performing the process, leading to slightly overestimated 8h TWAs.

Data obtained applying Strategy 1 are suitable to be compared to OEL at the group level (HEG) to decide whether workers are high, medium or low exposed, but no information to be used for risk management is provided.

The logbook method provides data, which can be used for compliance with OEL at individual level as well as at group level. Data obtained applying the logbook method can be used for risk management to control workers individual exposure level. An important advantage applying the logbook method is that quantitative data are obtained which can be used for decisions on intervention as shown in the present paper (Figure 16a , Figure 16b, Figure 17 and Table 6).

In an economically perspective, Strategy 2 in which **PC**s are measured by an occupational hygienist seems to be more expensive compared to Strategy 1 and Strategy 3. Applying Strategy 1, measurements can be handled by workers themselves (SAE), and only a couple of samples per worker are needed.

A method for estimating workers exposure (Strategy 3) has been proposed by Nyeland et al. (Nyeland *et al.*, 2002b) and applied in the present paper. Sampling is done using passive samplers as 8h TWA measurements plus logbooks. Sampling can be done by workers themselves as 'Workers Self Sampling' ('the WSS-Logbook method'). **PC**s are calculated from logbooks and 8h TWA measurements as a general linear model. The economical costs using this version of the logbook method are reduced compared to the traditional logbook method, Strategy 2, because the measurement procedure for obtaining the measurements has been simplified. In the present paper it is shown, that it is possible to obtain estimates of **PC**s matching the value of measured **PC**s with uncertainties in the same magnitude. In addition the need for an occupational hygienist presence during sampling is reduced, when using the WSS-Logbook method. The method is appropriate for screening of exposures.

A large number of estimated 8h-TWAs at a low cost can be obtained using the 'WSS-Logbook method' or logbook methods in general as in the present study (Figure 16a, 16b and 17). Logbooks

are handed out in the start of the logbook period and collected in the end. A way to improve the logbook method further is to introduce electronic logbook registrations. The WSS-Logbook method can be applied for measuring exposure to other contaminants than the ones studied in the present paper. The method is applicable when measuring exposure to all kinds of airborne agents - chemical or biological. The only requirement apart from the ones mention above (that the columns in the logbook-matrix are linearly independent), is that the sampling method has to be simple and easy to handle. Otherwise an occupational hygienist has to be present to assist during sampling.

When the purpose of performing an exposure assessment is to obtain data for estimating workers exposure to be used for a monitoring program, the strategies discussed in the present paper supports one another very well. When measuring on a population, both Strategy 1 and the logbook strategies provides data to answer the question, which workers are too high exposed at group level. This information can be used for decisions on general improvements such as general ventilation, general improvements on personal protective equipment for the HEG or substitution. The logbook methods identify exposure from processes performed and provide quantitative data for decisions on improvements. Such data are useful in case the intention of the exposure assessment is intervention to bring exposure under control at the individual level, e.g. the working pattern for the individual worker or emission from a process can be changed to reduce exposure.

CONCLUSIONS

- All strategies applied provide information on exposure at group level
- Applying Strategy 2 and Strategy 3, more accurate estimates of the long-term mean exposure value at the individual level are obtained compared to Strategy 1.
- In addition, Strategy 2 and Strategy 3 provide quantitative information useful for decisions on interventions, information useful e.g. for bringing exposure under control.
- Strategy 3 can be applied obtaining estimated **PC** associated with uncertainties in the same order as **PC** measured. Sampling can be done by workers themselves (SAE). There is an economic benefit in applying Strategy 3, compared to the traditional logbook method (Strategy 2) because the consumption of occupational hygienist time at the workplace can be reduced. Strategy 3 is adequate for use as a screening method.

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Paper [D]

EXPOSURE TO INK-FLY IN TWO DANISH HEATSET PRINTING SHOPS

[D] EXPOSURE TO INK-FLY IN TWO DANISH HEATSET PRINTING SHOPS

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ABSTRACT

Exposure to ink fly in two Danish heatset printing shops has been estimated using the Logbook Method. Due to the very high speed in heatset printing today, small droplets of ink (ink fly) are formed and made airborne. Pigment Yellow 12 and 13 (PY12 and PY13) are used as indicators of exposure to pigments in heatset printing.

Total amount of dust were sampled during a period of 24 hours, using a stationary high volume sampler and analysed for yellow pigment using HPLC with optical detection at 320 nm. Time Weighed Average Concentrations (TWAC) of exposure to PY12 or PY13 for each person were estimated. During a period of three weeks, workers were asked to fill in logbooks on time intervals for stay in three different locations (Machine Room, Control Room and Elsewhere) during working day. The amount of yellow pigment in the Control Room and Elsewhere were found to be less than the limit of quantification (0.33 $\mu g\ m^{-3}$) in the two companies investigated. The concentrations of yellow pigment in the Machine Room were, for all measurements above 0.33 but less than about 10 $\mu g\ m^{-3}$. A slight difference in the concentration level at the two companies was observed. The amount of yellow pigment was found to be 5% of total dust.

The estimated daily exposures of each worker during a period of three weeks were approximately log-normally distributed. For subjects included in the study, the mean exposure for PY during a period of one year was estimated to be 0.193 ± 0.091 mg $year^{-1}$ for a person working at Factory 1 and 0.051 ± 0.016 mg $year^{-1}$ at Factory 2. In comparison with the occupational exposure limit (OEL) of organic dust (3 mg m^{-3}), a value of C/OEL was found to be approximately 0.0006 ± 0.0004. It is concluded, that the measured exposure levels to yellow pigments for both the heatset printing shops investigated were extremely low compared with OEL.

Data was collected using different strategies to estimate individual TWAC. Data obtained from the different strategies are compared and discussed. Models to describe exposure observed at the factories are proposed. A mean value of exposure dose through a year on the factories investigated was estimated for each strategy used.

Keywords: Exposure assessment, aerosol sampling, 3,3'-dichlorobenzidine, logbook method

INTRODUCTION

In the printing and painting industry yellow pigments based on 3,3'-dichlorobenzidine (DCB) are used in a large amount. Pigment Yellow 12 (PY12), CAS 6358-85-6, and Pigment Yellow 13 (PY13), CAS 5102-83-0, are some of the most commonly used pigments. Due to the very high speed in heatset printing today, small droplets of ink (ink fly) are formed and made airborne to be inhaled by workers. The chemical structure of PY12 is shown in Figure 1. Physical chemical properties of PY12 and PY13 are very similar.

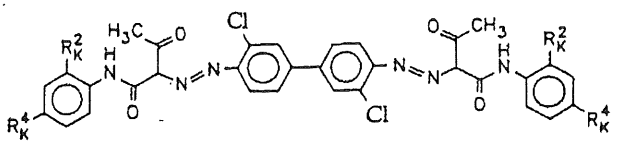

Figure 1.
Molecular structures of the 3,3'-dichlorobenzidines (DCB), PY12 a PY13.
For PY12, R_K^2 = H and R_K^4 = H, for PY13 R_K^2 = CH_3 and R_K^4 = CH_3 (Herbst *et al.*, 1997)

In theory, these pigments may be cleaved by azoreductases in the intestines or in human tissues and metabolised to the compound DCB, which is suspected to be a possible human carcinogen. Use of these pigments have been considered of no risk due to the fact that these pigments are insoluble in water and plasma, and thus not suspected to be absorbed in humans.

Some reports have indicated that workers in the printing industry have a higher incidence of cancer (Andersen *et al.*, 1999), primary in the gastrointestinal region, in the liver, lung and bladder. Urine samples from 36 workers exposed for DCB derivates were screened for aromatic amines (Hatfield *et al.*, 1992). No trace of DCB or monoacetyl-3,3'-dichlorobenzidine were found when analysing specific for these compounds (detection limit: 0.2 ppb).

The bioavailability of DCB pigments has been investigated in several animal studies. In inhalation, feeding and dermal studies the bioavailability was extremely low, with almost no systemic exposure to DCB pigments (Anonymous, 1995).

Data from a study by Prival et al. indicate that PY12 is not mutagenic primarily due to insolubility (Prival *et al.*, 2000). Carcinogenic effects of PY12 have been investigated as well (Leuschner, 1978). No significant carcinogenic effect of the pigments was observed.

It has been observed that metabolites of PY12 (mono substituted and free DCB) are highly mutagenic (Lazear *et al.*, 1979; Prival *et al.*, 2000) and that metabolites, primarily free DCB are carcinogenic (IARC working group, 1999).

Human exposure concentrations to PY 12 and 13 in the working environment have not been reported previously. In the present study, we report exposure to DCB and discuss different strategies applied for data collection and handling. Often when measuring exposures in the occupational environment, it is not possible to perform all measurements needed to measure exposure of all individuals studied. Often the occupational hygienists have to deal with missing data. The most straight forward strategy for estimating exposures in the present study would be to measure the concentration in the Machine Rooms for each day, match and multiply these values during the logbook period with logbook data (exposure time measurements). Because only one stationary sampler was available, it was not possible to measure concentrations in the Machine Room for all days during the logbook period. A complete data material for calculating exposure applying the straight forward, matched strategy does not exist. If only matched data were used, data from log days without concentration measurements would be lost.

The best estimate for the concentration in Machine Room on days when measurements were missing is the mean value of all measured days. An alternative strategy for estimating exposures for the logbook days with concentration measurements missing could be to use this arithmetic mean (AM) value to estimate exposures. If it was desired to use all logbooks collected, a reasonable strategy would be to use the time measurements from logbook days matching days where concentration measurements were obtained combined with AM values for days not matching.

It is important to keep in mind, what consequences choice of data set for estimating exposure has on data analysis and results. In the present script the dependence of choice of data set on results and analyses was studied. The effect of including outliers in data and how this can result in misleading results is also discussed.

Hypotheses:

- Daily working pattern are expected to be the same every day. Due to the high costs of the big printing machines, production is supposed to be in a high speed, steady and constant through the year. Variation in time spent in the Machine Room through

a working day, is supposed to be randomly, symmetrically distributed, and approximately normally distributed.

- Variation in concentration in the machine room is supposed to be approximately normally distributed, due to the constant production.
- It is appropriate to use a strategy mixing concentration data obtained applying different strategies, multiplying logbooks (exposure time measurements) with measured concentrations or AM of concentrations.
- Outliers may lead to incorrect results and conclusions.

The objective of the present paper was to estimate exposure for 3,3'-dichlorobenzidines during a year at the individual level depending on sampling strategy, using the logbook method.

MATERIALS AND METHODS

Study group

33 subjects were included in the study, 24 subjects from Factory 1 and 9 subjects from Factory 2. All subjects were males, except one female in Factory 1. Range of age was 21-61. There were three work shifts (day, evening and night shift) in Factory 1. Each worker had a specific job title: First printer, second printer, third printer and helper. A strictly hierarchic structure of the work was observed at printing shop 1. In printing shop 2 workers were working in two-shift operation (each of 12 hours). The work was not as strictly hierarchic structured as in printing shop 1. During the reference period, all workers at both the factories were working at all shifts due to rotations.

Exposure measurements

Exposure for total dust and PY12 or PY13 was estimated for workers in two heatset printing shops. The Logbook Method (Olsen, 1994; Olsen *et al.*, 2002) was used to estimate the individual daily exposure by measuring the air concentration (C) (stationary samples in different areas) multiplied by exposure duration (T) (exposure time measurement) registered in logbooks by the workers.

Each printing shop was divided into three areas, in which workers spent their time during the working day, the Machine Room (containing the printing machines), the Control Room (from which the machines were controlled) and Elsewhere (other places such as cantina, toilet etc.). The three rooms were supposed to contain different levels of exposure to the pigment. The Machine Room and the Control Room were separated with self-closing doors. Pressure was kept high in the Control Room.

In printing shop 1, two machines (1A and 1B) were printing simultaneously in each of two Machine Rooms controlled by two teams of workers working in parallel. The printing ink used at the machine 1A in printing shop 1 was 'Premium Yellow' from SunChemical containing PY12. At machine 1B, in printing shop 1, the printing ink was 'Premoterm Heatset web offset ink' from Manders-Premier containing PY13.

In printing shop 2 workers were working in two-shift operation (each of 12 hours). The work was not as strictly hierarchic structured as in printing shop 1. The printing ink used in at the machine in printing shop 2 was 'Premoterm Heatset web offset ink' from Manders-Premier containing PY13.

Process concentrations

Total dust was sampled at a rate of 22,5 m^3/hour using a stationary, High Volume Sampler (Gravicon VC 25). Dust was collected on fibre glass filters (Sartorius AG, no. 13400-150—K, d=15 cm). Sampling period was approximately 24 hours.

For each sampling day the sampler was placed in either the Control Room (by the control desk, where workers were spending most of the time) or in the Machine Room, by random selection. In the Machine Rooms the sampler was placed close to the printing machine containing the yellow printing ink at the place, where we supposed to sample air containing the highest level of yellow ink fly. In this case, the stationary sampling would represent 'worst case' sampling, assuming to sample the highest level of exposure for yellow printing ink in the room.

Filters were analysed for content of pigment yellow 12 and 13 by HPLC/UV-VIS spectroscopy.

Extraction and analysis of filters

Chemicals: Dichloromethane p.a., dichlorobenzidine p.a., acetonitrile p.a. Pure preparations of PY12 and PY13 for analysis were a gift from Dr. Reinhardt Jung, Clariant GmbH, Frankfurt am Main, Germany.

Each filter was cut into small pieces (0.5 cm^2) and blended in dichloromethane. This blended substance for each filter was placed on ultrasound bath for half an hour. Subsequently the solution was filtered through a GFC glass filter to a flask. The final volume was 200 ml. Before analysis, 2 ml of each solution were evaporated and dissolved in 2 ml dichlorobenzidine. Each sample was analysed by straight phase HPLC (Hibar LiCrosorb Silica 60 (5μm), 25 cm; 1 ml/min; 3% acetonitrile in dichlorobenzidine) equipped with a UV-VIS detector. Detection was at λ = 430 nm. Injection volume was 50 μl. The recovery of PY12 and PY13 were determined by inclusion of standard filters with known amounts of the pigments suspended in paraffin oil.

According to the evaluation of the method recovery for PY12 was 77% and 61% for PY13. LOQ was reported to be 0.33 μg m^{-3} (personal communication, Håkan Wallin, 2001-03-25).

Logbook measurements

The workers were asked to fill in logbooks for a period of 15 working days. The exact time of entering or leaving the areas was logged, as well as name, date, shift and comments if necessary. A reprint of the top of the logbook for printing shop 1 is shown in figure 2.

Exposure was estimated as Time Weighed Average Concentration (TWAC) during a working day (8 hours in Factory 1 and 12 hours in Factory 2) for each person, according to the Logbook Method (Olsen, 1994; Olsen *et al.*, 2002). Data were handled and analysed in SAS statistical software, version 8.2.

Name				**Machine no.**		**Day Shift** *X*	**Date**
Mr. X				*01*		**Evening Shift**	*02-02-01*
						Night Shift	
Control room		**Machine room**		**Elsewhere**		**Comments**	
In	**Out**	**In**	**Out**	**In**	**Out**		
07:00	*07:20*	*07:20*	*07:35*				
07:35	*08:30*			*08:30*	*09:05*		
09:05	*10:30*	*10:30*	*11:00*	*11:00*	*11:10*		
11:10	*12:45*			*12:45*	*13:15*		
13:15	*13:55*	*13:55*	*14:10*				

Figure 2. Upper part of logbook from measurements in Factory 1

Strategies applied

Three kinds of strategies: Strategy A, Strategy B and Strategy C were applied to calculate TWAC, for measurements at each factory (Table 1). The strategies were based on exposure time measurements (logbooks) and concentration values as described in Table 1.

Table 1. Strategies applied to estimate TWAC.

Strategy set	Time Measurements	Concentration	Comment
Strategy A	Logbooks matching days for measured concentrations	Measured concentrations	Measured C and measured T, strictly matching
Strategy B	Logbooks not matching days for measured concentrations	AM of measurements	Measured T, where C is missing
Strategy C	Logbooks for all days	Measured concentrations and AM for days where no measurement was obtained	Strategy A and Strategy B applied (data1 and data2 concatenated)

AM: Arithmetic mean; C: Concentration of DCB in Machine Room (μg m^{-3}); T: Exposure time measurement

For Strategy A individual TWACs were obtained directly as estimated by the logbook method, using only the logbooks (exposure time measurements) and the Machine Room concentrations measured, matching the logbook days.

To compensate for missing data of Machine Room concentrations, the mean values of the measurements obtained the other days, were used to estimate exposure for the logbook days, with no Machine Room measurements. This was done in Strategy B, exclusively based on AM-values of Machine Room concentration in each of the factories and logbooks for days with missing Machine Room measurements. This strategy was thus based on logbooks not matched using Strategy A. Strategy C is a concatenation of data obtained using Strategy A and Strategy B.

No concentration level above the detection level of PY12 or 13 was observed in the Control Rooms in either Factory 1 or Factory 2. For all estimations of TWAC, concentration of yellow ink fly in Control Room and Elsewhere were assumed to be equal to 0 μg m^{-3}.

RESULTS AND DISCUSSION

No analytical quantifiable amounts of PY12 or PY13 were observed in any samples from Control Room and Elsewhere in any of the factories. The level of PY12 or PY13 in the Machine Rooms, sampled during a time period of 24 hour during the reference period of 22 days, was extremely low, about 0.47 – 10.4 $\mu g\ m^{-3}$ (Figure 3). The concentrations in the Machine Rooms, were found to be normally distributed, which was tested by using a Kolmogorov-Smirnov normality test ($p>0.15$), using the statistical software MINITAB version 13. No significant difference in exposure level at the two machines 1A and 1B using PY12 and PY13 at Factory 1, was found (a two sample t-test, $p=0.53$).

One measurement in the Machine Room at Factory 2 was far above the others of the measurements from this factory (about 10 times greater than on other days) resulting in the higher mean value and a large standard deviation. No obvious explanation for this was observed. Due to the high costs of the printing machines, production is at high constant speed 24 hours a day throughout the year. It is not possible to raise the printing speed 10 times in shorter periods compared to other production days. It was decided to include this measurement in the data material of Factory 2, to study the effect of including and excluding an outlier.

A significant difference was observed in concentration level between the two factories. When including the high value measured in Factory 2 (the outlier), the mean concentration level of ink fly in the Machine Room ($AM=2.19 \pm 3.62\ \mu g\ m^{-3}$) is higher than the mean concentration level in at Factory 1 ($AM=1.71 \pm 0.84\ \mu g\ m^{-3}$). When the high value in Factory 2 is excluded ($AM=0.82 \pm 0.22\ \mu g\ m^{-3}$) and the level in Factory 2 turns out to be lower than in Factory 1.

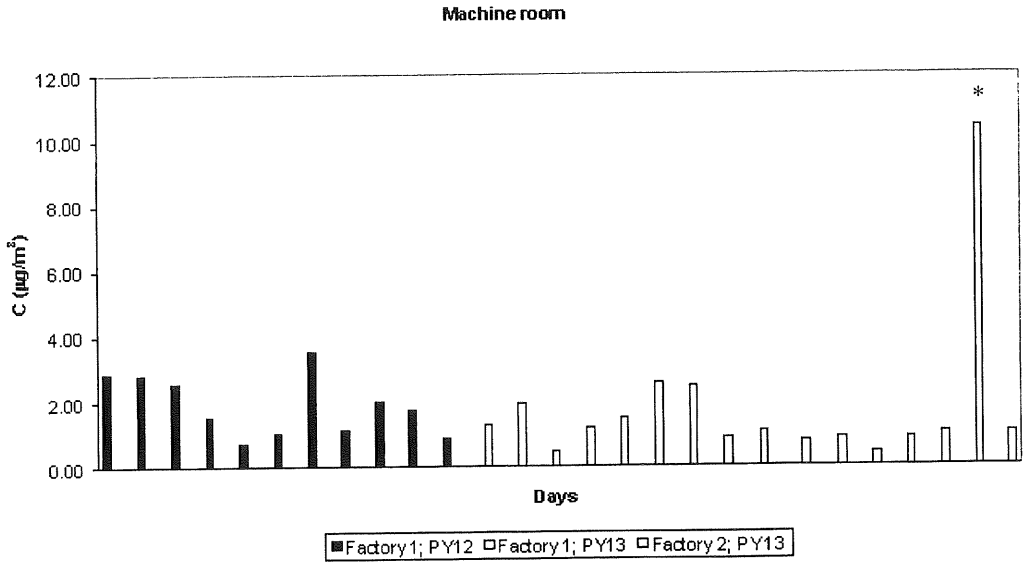

Figure 3. Concentrations in the Machine Rooms (Process Concentrations) at Factory 1 and 2. * indicates the 'outlier'.

To illustrate the risk when only measuring one day, mean values of estimated TWAC, for persons working at Factory 2, calculated the day where the high value was obtained are compared to a mean of TWAC the other days during the logbook period (Table 2). TWAC is calculated using the data obtained using Strategy A. The difference in estimated TWAC this day compared to the other days (a factor of three) illustrates, that exposure level can vary largely in the working environment from day to day. It is not enough to measure only one day to get reliable data for estimating exposure during a longer period, for instance a year.

Table 2. Mean TWAC on a high-production and a 'normal' day at Factory 2.

High-prod. day TWAC mean	SD	'Normal' day TWAC mean	SD
µg m^{-3}	µg m^{-3}	µg m^{-3}	µg m^{-3}
0,215	0,006*	0,066	0,033

*Within one day

The fraction of time spent in the Machine Room for each worker registered in the logbooks in the period investigated, were log-normally distributed for the majority of the subjects (Table 3). Based on logbook data fraction of time spend in Machine Room on each working day during the logbook period for each worker were tested for normality and subsequently for log-normality using a Kolmogorov-Smirnov normality test (P>0.15).

The amount of time spent in the Machine Room relative to the total time of a whole working day for each person at Factory 1 and 2 is shown below (Figure 4). It seems that the working patterns in Factory 1 and 2 differ. Relatively, workers at Factory 2 were spending less time in the Machine Room during working day compared to the workers at Factory 2.

Table 3. Time spent in Machine Room through a working day for individuals during the logbook period. Tested for normality vs. log normality using a Kolmogorov-Smirnov normality test (P>0.15).

Normal distributed	Log normally distributed	Neither normally nor log normally distributed
63%	84%	13%

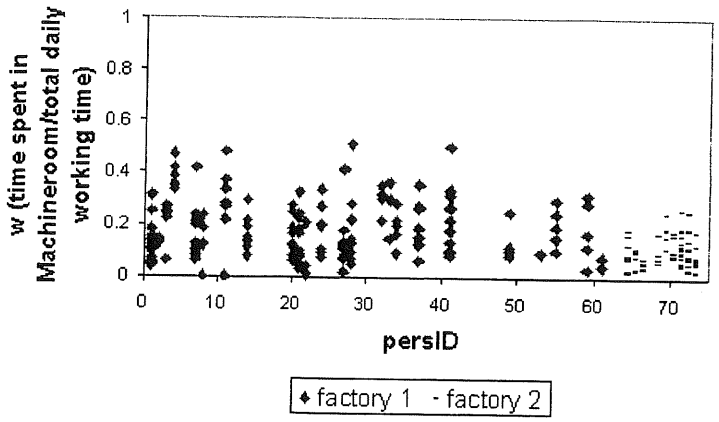

Figure 4. Fractions of time spent in Machine Room during working day in Factory1 and Factory 2.

Mean values of TWAC, calculated from the three data set generated, are shown in Table 4. The dose per year was calculated. Data were obtained applying the strategies described in the section 'Strategies applied' above.

For Factory 1 when applying Strategy B and Strategy C, AM=1.49±0.70 $\mu g/m^3$ of Machine 1A and AM=1.88±0.94 $\mu g/m^3$ of Machine 1B in the Machine Room.

For Factory 2 data were obtained with and without the high value measured on one of the days. Excluding the 'outlier', AM=0.82±0.22 $\mu g/m^3$, and including the 'outlier' AM=2.19±3.27 $\mu g/m^3$, when applying Strategy B and Strategy C.

Table 4. Calculated mean values of TWACs for persons working at Factory 1 and Factory 2. Results obtained applying Strategy A (strictly matched), Strategy B (mean values) and Strategy C (concatenated) are listed. Estimated dose per year for a person working at Factory 1 or Factory 2 were calculated.

Factory	Strategy	TWAC mean $\mu g/m^3$	SD $\mu g/m^3$	Dose per year μg	SD μg
1					
	Strategy A	0.3468	0.2558	780.3	575.6
	Strategy B	0.2797	0.1948	629.3	438.4
	Strategy C	0.2977	0.2143	669.7	482.1
2					
'outlier' excluded	Strategy A	0.0660	0.0333	148.5	75.0
	Strategy B	0.0533	0.0315	119.9	70.9
	Strategy C	0.0585	0.0326	131.7	73.4
'outlier' included	Strategy A	0.0814	0.0559	183.2	125.8
	Strategy B	0.1199	0.0709	269.8	159.5
	Strategy C	0.0656	0.0458	147.7	103.0

Comparing the data sets for Factory 1 (considering possible effects due to machines, shifts and job status) no significant difference between the data sets was found, using analysis of variance. It seems as if the concentration (average or matching) does not have a great impact on variation in data, when comparing the data sets. No matter if different measurements were used as concentration (Strategy A) or a mean value is used as concentration (Strategy B), no significant difference was observed. Time measurements from the logbooks appeared to be the most important source for contributing to the variance. The variance (V) of exposure dose (D) can be described:

$$D = CT \qquad (1)$$

$$log(D) = logC + logT$$

$$\frac{V[D]}{(E[D])^2} \cong \frac{V[C]}{(E[C])^2} + \frac{V[T]}{(E[T])^2} \qquad (2)$$

Using that: $V[\log X] \cong \frac{1}{E[X]^2} V[X]$.

E is the mean value.

In these data, the relative variance of C was much smaller than the relative variance of T.

For Factory 2 it seemed that it is of great importance whether the 'outlier' was included or not. In the case the 'outlier' was not included, the variation was reduced but no significant difference could be observed between the three data sets. Strategy C is an appropriate and suitable way of estimating exposure given data obtained. Including the 'outlier' leads to a more doubtful conclusions. It was decided to exclude the high measurement in further analysis, considered as an outlier due to preparation or analysis.

Data obtained applying Strategy C for Factory 1 and Factory 2 (without the 'outlier'), was considered to be an appropriate way of reflecting the actual exposure – at least the best one, given the circumstances during sampling. Data obtained applying Strategy C was used for further analysis of exposure data below.

The majority of the estimated exposures (TWACs) from day to day were log-normally distributed for almost all subjects in of both factories applying Strategy C. Concentration measurements from the Machine Rooms in both factories were normally distributed from day to day, and the time intervals noted in the logbooks were log-normally distributed. When combining C and T, the estimated individual exposures turned out to be log-normally distributed, reflecting the differences in the working pattern. This is not expected, when considering that the factories production were supposed to be much the same from day to day during the year, as we proposed in the hypothesises.

In the literature it has been reported that individual exposure to chemical substances in the working environment in general usually are log-normally distributed between days (Rappaport, 1991; Roach, 1992). In Figure 5 the arithmetic means (AM) of each subject investigated are shown. The log transformed standard deviations (SD) are shown as well. An overall difference in concentration levels of Factory 1 and 2 was observed.

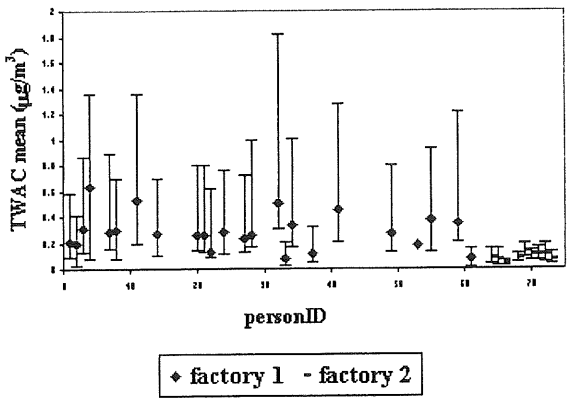

Figure 5. Arithmetic means of TWAC of working days during the logbook period, for individuals at Factory1 and Factory 2. Log transformed standard deviations are shown.

No specific occupational exposure limit (OEL) exists for 3,3'-dichlorobenzidines. To assess the level of exposure, OEL of exposure to organic dust in general (3 mg m^{-3}) has been used. In Figure 6 the values of C/OEL of all subjects are shown. Log transformed SD are shown as well. Exposure level at the two factories differs in which the level at Factory 2 is below the level at Factory 1. In this context, when compared to the OEL of exposure to organic dust, it is clear that the values of exposure are extremely low at both factories studied.

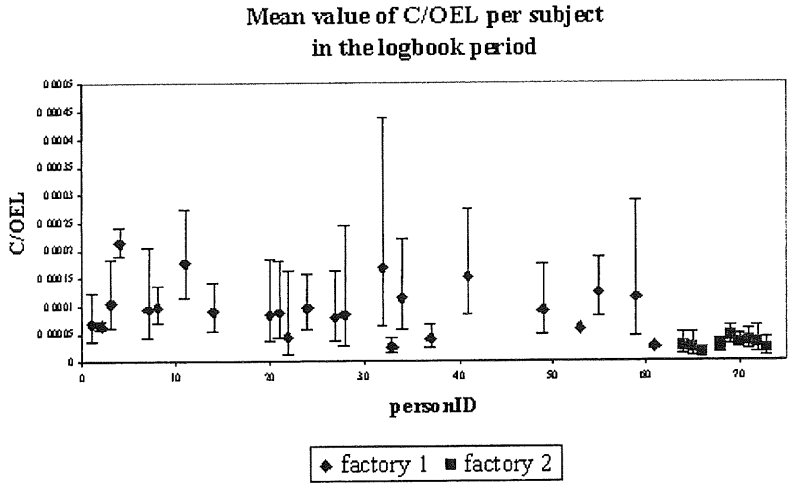

Figure 6. Arithmetic mean values of exposure to PY12 and PY13 of individuals compared to OEL of organic dust (3 mg/m3).
Log transformed standard deviations are shown.

Analysing and modelling exposure

Data from Factory 1 was analysed to investigate how exposure was influenced by:

- Type of Machine (1A, 1B)
- Shift (day, evening, night shift)
- Job title (First Printer (FP), Second Printer (SP), Third Printer (TP) and Helper (H)).

A model of the exposure (TWAC) was designed as a systematic, crossed, three sided variance analysis, for Factory 1:

$$Y_{ijkl} = \mu + a_i + b_j + c_k + ab_{ij} + ac_{ik} + bc_{jk} + abc_{ijk} + Z_{v(ijk)} \quad (3)$$

Where μ is a general level, a_i is difference from the general level of the i´th machine, b_j is the difference from the general level of the j´th shift, c_k is the difference from the general level of the k´te job title and $Z_{v(ijk)}$ is the residual. The combination of a, b and c indicates interactions.

Analysis of variance was performed in SAS statistical software, using General Linear Model (PROC GLM).

When analysing data3 (obtained applying Strategy C) exposure difference due to job status was significant (<0.0001). Helpers were more exposed than the other three job categories. This reflects the working pattern observed during working day. First Printer was spending most time in the Control Room, controlling the machine. Second Printer, Third Printer and Helper were usually spending more time in the Machine Room by the Machines. No interactions are found to be significant. For data3 the model is reduced to:

$$Y_{ijkl} = \mu + c_k + Z_{v(ijk)} \quad (4)$$

In Factory 2 data were analysed for differences in exposure of shifts (day and night shift). Only one machine was printing yellow printing ink. Since workers did not have strict job titles and status as in Factory 1, it was not possible to differentiate individuals according to this category. No significant difference was found between the two shift (day and night) at Factory 2, by a two sample t-test.

Due to the difference in working shift (3×8 h-shift and 2×12 h-shift) at the factories, a suitable way to compare exposure to ink fly, at Factory 1 and 2, will be to compare values of exposure dose for each individual through a year. Different numbers of working days throughout a week at Factory 1 and 2 are taken into account. Estimated, individual exposure doses through a year are shown in Figure 7.

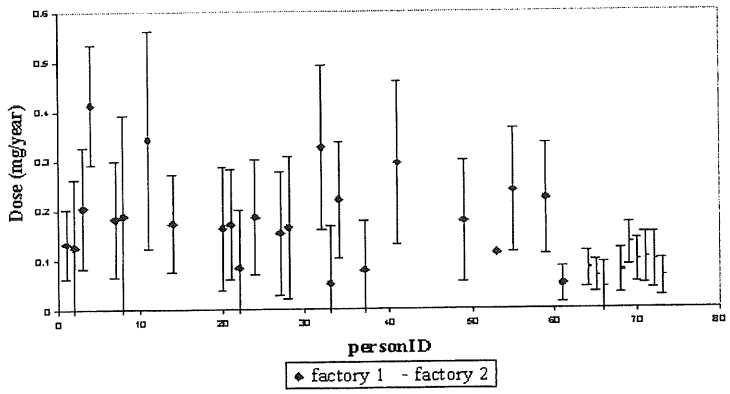

Figure 7. Exposure dose at individual level of exposure to PY12 and PY13 during a year in Factory 1 and Factory 2.

The mean value of exposure for 3,3'-dichlorobenzidine of a person during one year, no matter of type of machine, shift or job title is shown in Table 5 below. It was concluded that the exposure for 3,3'-dichlorobenzidine was higher in Factory 1 than in Factory 2. This difference could be due to better ventilation facilities in Factory 2 compared to Factory 1. Factory 2 is a new company with more modern equipment. For both of the factories the exposure seems to be extremely low compared with OEL for organic dust in both companies.

Table 5. Mean dose value of exposure to PY12 and PY13 during one year for a person working in Factory 1 or 2.

	Dose (mg/year) ± SD
Factory 1	**0.193 ± 0.091**
Factory 2	**0.051 ± 0.016**

CONCLUSIONS

Exposure for 3,3'-dichlorobenzidine is extremely low in the heatset printing industry. The low concentration of aerosols in the air is probably because the inks are very highly viscous, which may lead to a low degree of formation of ink fly. The content of pigment aerosols in the air inhaled by the workers may thus be very low.

The present study might be used as a model for exposure assessment to organic dust or aerosols in general in the occupational environment using the Logbook method. A similar method could be used to estimate exposure for e.g. red and blue pigment or carbon-black.

It is surprising that the time measurements showed that variation in working pattern is log-normally distributed in the logbook period. The hypothesis about working pattern in the printing industry, being normally distributed through a longer period, cannot be maintained. Concentration of DCB in the Machine Room was found to be approximately normally distributed. The hypothesis in the introduction was thus not rejected. An appropriate way of estimating exposure, based on the data obtained in the study, was found to be concatenating the matching data (logbooks and measured concentration) with logbooks for the other part of data using AM as estimates for concentration in Machine Room. The outlier value measured in Factory 2, actually seemed to influence the result. It is of great importance to be aware and conscious about outliers. Outliers can lead to incorrect results and conclusions.

The estimated exposure doses during a year received by a worker, indicates that workers at Factory 1 receive a higher dose compared to workers at Factory 2.

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Paper [E]

EXPOSURE ASSESSMENT AND INTERVENTION – BRINGING EXPOSURE UNDER CONTROL

[E] EXPOSURE ASSESSMENT AND INTERVENTION - BRINGING EXPOSURE UNDER CONTROL

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ABSTRACT

A procedure for bringing workers exposures under control on company level, in a specific line of industry or nationwide, is described and discussed.

For exposure assessment at the individual level, measurement strategies such as the logbook method (Strategy 2) (Olsen, 1994) and an extended version of the logbook method (Strategy 3), proposed in this paper, are adequate. These methods provide quantitative data for improvements in the workplace and interventions at process level, based on information on process concentrations and the time spent at each process. Depending on the size of the population investigated, it is decided which strategy to choose. Strategy 2 is suitable for both smaller and larger populations, but an occupational hygienist must be present during sampling, when measuring **PC**, and partly during the log period.

Strategy 3 is suitable for larger populations and work pattern (time spent at the processes) should preferably be such that the columns in the logbook-matrix are linearly independent. Passive sampling, done by workers themselves (SAE), can be used. A new word is introduced: WSS (Workers Self Sampling), which better describes what is going on. Workers are not assessing but sampling exposure. Strategy 3 (the WSS-logbook method) is appropriate to be used as a screening method.

Keywords: Exposure assessment, intervention, sampling strategy, logbook method

CONTENTS

1. INTRODUCTION
   1.1. Worker welfare
   1.2. Hazard, exposure and risk – Risk assessment in general
      1.2.1. Hazard assessment
      1.2.2. Exposure assessment
      1.2.3. Estimation and characterization of risk
   1.3. Exposure assessment, background information
   1.4. Conclusions on background information
   1.5. Objective

2. DESCRIBING THE PROBLEM
   2.1. Bringing exposure under control
      2.1.1. Decision rules
      2.1.2. Concluding remarks
   2.2. Considerations on variability in exposure
   2.3. Exposure and emission
      2.3.1. Time domain
      2.3.2. Process domain
      2.3.3. Exposure distributions (log normal)

3. METHODS
   Steps of bringing exposure under control
   3.1. Information and Screening 0
   3.2. Mapping and Screening 1
   3.3. Exposure assessment and Screening 2
   3.4. Intervention
   3.5. Exposure assessment (of intervention) and Screening 3
   3.6. Population monitoring

4. DISCUSSION

5. CONCLUSIONS

6. APPENDIX

7. REFERENCES

1. INTRODUCTION

1.1 Worker welfare

Health and safety authorities duty is to ensure that the working environment is satisfactory by controlling that no workers are exposed to a particular substance above Occupational Exposure Limits (OELs) in force. OELs refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be exposed repeatedly to the given substance day after day without experiencing any adverse effects (ACGIH, 2002)). OELs are based on available information from industry, from human and animal experimental studies or from a combination there off. Risk for adverse health effects due to chronic exposure at the workplace is assessed by comparing data on long-term exposures with the OELs. To ensure, that the welfare of the workers nation-wide is not endangered it is desirable to perform an exposure assessment followed by interventions if needed in a given line of industry, a given company or a given department as the first step to bring the exposure under control. This could be done by introducing interventions at the group level to lower the level of exposure e.g. by substitution of a hazardous substance with a less harmful one or by enhancing ventilation in a working room. It can also be done at the individual level for instance by changing specific processes or changing the local surroundings of a process (e.g. local exhaust ventilation). Depending on the purpose of the exposure assessment a suitable strategy should be chosen.

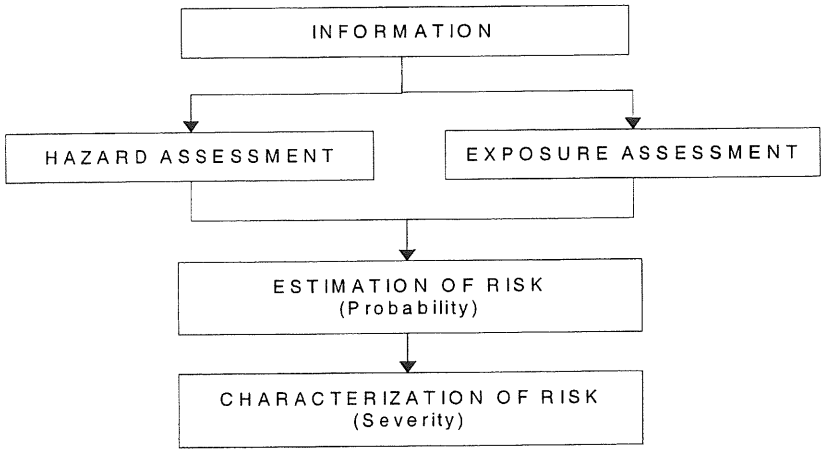

Figure 1. Model of risk assessment as used in the EU (EU, 1994)

1.2. Hazard, exposure and risk – Risk assessment in general

Hazard assessment and the exposure assessment form the basis of estimating and characterizing the risk as illustrated in the model used in the EU (Figure 1) for risk assessment.

1.2.1. Hazard assessment

Hazard assessment is a process in which elements from a hazard analysis are combined and assessed. It is the identification and quantification of the adverse effects a substance may cause on those exposed. A list of substances, which may constitute a danger of adverse health effects for the worker, is the first step of an identification of a hazard at the workplace. Hazard is a property of the substance. The source of hazard may be divided into parts, which can be studied separately. Potency of the particular substance or hazard has to be determined. Potency is a measure of how small a dose of a toxic chemical is needed to trigger an adverse effect in an organ. Potency of the hazard can be assessed ordinally or quantitatively.

OEL of a particular substance can be derived from NOAEL or LOAEL to get a quantitative acceptable level of exposure to the substance. American Conference of Governmental Hygienists (ACGIH) made one of the earliest moves towards this kind of quantitative criteria to judge acceptability of measured exposure levels by introducing TLV (Threshold Limit Values)(ACGIH, 2002). According to the ACGIH three categories of TLVs are specified:

1. Time-Weighed Average (TLV-TWA) – the time-weighted average concentration for a conventional 8-hour workday and a 40-hour workweek, to which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect.
2. Short-Term Exposure Limit (TLV-STEL) is defined as a 15-minute TWA exposure, which should not be exceeded at any time during a workday even if the 8-hour TWA is within the TLV-TWA. Exposures above the TLV-TWA up to the STEL should not be longer than 15 minutes and should not occur more than 4 times per day.
3. Ceiling (TLV-C) is defined as the concentration that should not be exceeded during any part of the working exposure.

In the United States of America Action Level (AL) is defined as 0.5 × TLV, a level where action (some kind of intervention) has to be carried out.
Interpretations from the hazard analysis form the basis of the hazard assessment.

1.2.2. Exposure assessment

Exposure assessment may be based on measurements of exposure concentrations in the working environment or by predictions of a concentration level using models. The assessment may include past or current exposures. The result of an exposure assessment reflects a person's or group of person's exposure to a given source of hazard (e.g. expressed as the mean value of concentration) during a certain time interval. When making an exposure assessment it is important to decide:

What to assess, when to assess, the representativeness of measurements and the reliability of measurements (Herber *et al.*, 2001). Reliability depends on the strategies for sampling, analysis and protocol as well as adequacy of the technique being used as indicated in chapter 1.3. Good quality of data is essential. Representativeness of measurements – Do measurements reflect exposure properly according to for instance location? - depends on choice of strategy for sampling (time of measurement, location and number of measurements).

1.2.3. Estimation and characterization of risk

Risk assessment is done by comparing hazard, exposure and the exposed people's sensitivity, which gives the risk of adverse health effects (probability). Risk characterisation is comparing the risk with seriousness of the consequences. Usually consequences are assessed, e.g. compared to OEL values. It is important to remind that a source of hazard does not constitute a risk

if nobody is exposed to it. Risk is a conditional probability e.g. the probability of adverse effect in a person or group of persons during a specific time interval and under certain circumstances. The degree to which the exposure level for a given compound exceeds the established safe exposure level is a measure of the risk. OELs are usually used for these assessments.

Risk assessment in the occupational environment makes it possible to assess the magnitude of risk of:

1. Working in a specific company in which the person is in contact with different substances during one or several kinds of processes. Considerations about background level must be included. Assessment done in a specific company.

2. Performing a given process. Assessment carried out across several companies.

3. Being exposed to a given substance. Assessment could be done across both processes and companies.

4. Selected types of jobs. Assessment in a specific line of industry.

Ideally, based on a vision of which information the investigation will produce, a suitable measurement strategy for one of the four possibilities above is selected. An overall experimental design is determined depending on the purpose of the investigation. These considerations lead to the final measurement tactic on how to sample (e.g. where to place the sampler, duration of sampling).

1.3. Exposure assessment, background information

The available exposure dose in the breathing air (E_{DA}) can be expressed as the product of the exposure concentration (C) and the exposure time (T), based on Haber 's rule (Haber, 1924):

$$E_{DA} = C\,T \qquad (1)$$

Exposure can be defined as the integral of the air concentration-time curve over the exposure period, equal to the true arithmetic mean (AM) air concentration during the period considered, times the duration of the period. Uptake in the lungs of a given contaminant is assumed to be proportional to the concentration in air inhaled by the worker (Rappaport, 1991). Uptake during a longer period of time e.g. during a year, is thus proportional to AM for that period. It is thus the long-term arithmetic mean air exposure concentration, which can be related to risk of adverse health effects due to chronic exposure for a single worker (Rappaport, 1991).

In quantitative exposure assessment mainly two different kinds of strategies are applied. The first is measuring at the individual level in which all members of a population are monitored. In the second approach the average level of a group's exposure is applied to all members of the group. In this case only a representative sample of the group are being sampled.

The most simple and most expensive way of performing exposure assessment is to measure all individuals considered during the time interval investigated. In most cases this is unrealistic for practical and economical reasons.

The first step in an exposure assessment of a group of workers in a time period is to delimit the group of people under investigation, and the integration time the exposure's being estimated (average daily exposure during a time period of n days). Choosing a suitable strategy depends on the purpose of the exposure assessment. One purpose could be to estimate the average exposure of the group over time. This strategy could be suitable for epidemiological studies. Another strategy could be to estimate the average exposure of individuals and compare this value to average exposures of e.g. other persons. This strategy is suitable for studies in occupational hygiene for improvements of the working environment under limited resources or determining compliance with OELs at the individual level.

Table 1. Comparing different sampling and measurement strategies for exposure assessment.

Strategy	Sampling	Measurand	Purpose	Level
Worst-case	Few, systematically selected persons	Concentration	Compliance *	Individual
'Measured 8h-TWA Strategy' (Strategy 1)	Several, randomly selected persons	Concentration	Intervention (overall) Epidemiology, Risk Assessment	Group
Logbook Method (Strategy 2)	Several, randomly selected persons	Time and Concentration	Compliance, Intervention (local), Epidemiology, Risk Assessment	Individual and Group

*When results are < OEL or STEL.

In the present paper four kinds of measurement strategies are considered. The sampling strategy suggested by European standard EN 689 called the 'worst case' strategy is a practical method for sampling without any theoretical base (European Commitee for Standardization (CEN), 1995). It is based on the principle that the occupational hygienist is choosing subjects to be measured on that are supposed to be exposed for the highest dose. Compared to random sampling it has been shown that 'worst case' strategy leads to higher values of exposures, it is biased with a factor of more than five (Olsen *et al.*, 1991). This strategy can be used for determining that the exposure concentration is below the OEL but cannot be used for demonstration of non-compliance with OEL. A high result may be caused by the 'worst case' situation or because the long-term average is above the OEL, or both (Olsen *et al.*, 2002). Because it is biased to an unknown degree, data cannot be used to establish OEL or for epidemiological studies.

A random selection of people can be stratified on the base of homogeneous exposure groups (HEG) (Rappaport, 1991) or similar exposure groups (SEG) (Mulhausen *et al.*, 1998). The population investigated is divided into groups supposed to be exposed for approximately the same concentration level. Criteria for this division could for instance be that the workers have the same job titles, are exposed to the same agents or that they are working in similar surroundings with the same kind of ventilation. Often it is seen that HEGs are inhomogeneous (Rappaport *et al.*, 1993) and it can be necessary to change strategy after a couple of preliminary measurements. Rappaport

defined a HEG to be a group of persons for which 95% of the individual arithmetic mean concentrations are within a factor of 2 (Rappaport, 1991):

$$R_{0.95} = \frac{e^{(\ln(GM)+1.96\ln(GSD))}}{e^{(\ln(GM)-1.96\ln(GSD))}} = e^{(3.92\ln(GSD))} = GSD^{3.92} < 2 \qquad (2)$$

A method referred to as the 'Measured 8h-TWA strategy' or Strategy 1 in this paper was proposed by Rappaport (Rappaport *et al.*, 1993). Data are analysed using the random effects model (Rappaport *et al.*, 1995) or with explanatory variables using mixed models (Nylander-French *et al.*, 1999; Rappaport *et al.*, 1999). Measurements can be performed as 8-hour measurements, handled by the workers themselves, SAE* (Self-Assessment of Exposure), distributed and collected by mail (Liljelind *et al.*, 2000). It is possible to estimate the average within and between worker variability, when at least two repeated measurements on each worker are carried out. Covariates contributing to the exposure can be included in the model. This method is described in more details below (Section 3 and Appendix).

An alternative method is the logbook method, where exposure concentration and exposure time are measured separately. The Process Concentration (**PC**) for each process during the production can be estimated, by measuring different operators performing the process. Exposure time is measured by the workers themselves, keeping logbooks on when they start and stop the different processes during the working day. A matrix for daily exposure concentration of each worker can be established based on **PC** (C) of each process performed during working days and the exposure time (T). Stratifying on the base of processes often results in a reduction of the variability in data, which has been shown by (Olsen, 1994). A higher degree of accuracy on the measurement result (a workers long-term average exposure) is obtained, because a larger number of estimates for daily exposures are obtained compared to Strategy 1. The logbook method is based on process domain and time measurements (logbook) on the contrary to the more traditional strategies as Strategy 1, in which exposure is measured in time domain (Olsen, 1994). Exposure estimates at the individual as well as at the population level are obtained. The logbook method is described in more details below (Section 3 and Appendix). A measurement method appropriate as screening method,

* SAE is not a suitable name for this kind of sampling. Workers are not doing any *assessment* - more correctly they are doing *sampling*.

based on the logbook method, called the WSS-logbook method is proposed in the present paper and described in Section 3.

1.4. Conclusions on background information

During recent years more focus has been put on occupational exposure assessment especially in the area of epidemiology. A need for more data and attention on sampling strategies to obtain the most reliable and unbiased data for exposure assessments has increased as well.

Different kinds of strategies depending on the purpose of the exposure assessment can be conducted. Generally, exposure can be assessed at the individual level or at the population level depending on the object of measurement.

Monitoring exposure in the occupational environment is a central task, to secure the welfare of the worker. Often there is lack of knowledge on exposure to both known and unknown substances in the occupational environment. Over-exposures should be identified and be brought under control. Monitoring exposure should ensure that exposure stays under control.

1.5. Objective

The objective of this work is to describe and discuss a procedure for bringing workers exposures under control on company level, in a specific line of industry or nationwide. When exposure has been brought under control, monitoring can prospectively secure, that exposure stays under control (Holst *et al.*, 2002).

2. DESCRIBING THE PROBLEM

2.1. Bringing exposure under control

Exposure can be brought under control either at population level or at individual level. Substitution of a product to lower or avoid exposure for a given compound could be introduced nationwide, in a given line of industry or in a company (i.e. at population level). A method for assessing exposure factors is calculation of SUBFAC index of each product used (Olsen *et al.*, 1992). SUBFAC index is the relative risk of exceeding the air equal standards in force during use of alternative products. When SUBFAC index is used as criteria, decisions about substitution can be made according to this value. To illustrate application of this method, e.g. substitution of dichloromethane (SUBFAC=14 558) with acetone (SUBFAC=576) reduces the relative risk of exceeding the limiting value by a factor of more than 25. When using the SUBTEC-software the rate of evaporation and OEL are used calculated in the units: [R]=g/min/m^2 and [OEL]=g m^{-3} respectively. These units cancel out when calculating the SUBFAC index.

Another example of how to bring exposure under control at the population level is to improve ventilation in a company, which may lower the level of exposure for all workers.

At the individual level, focus is on process or the emission from processes, the local environment or the operator of the process. Bringing exposure under control can be done at the local level such as changing process, shielding the exposed from the source, substitution of product, improvement of local exhaust ventilation, introduction or improvement of personal protective equipment.

It is important to 'followup' upon introduction of intervention to investigate whether the intervention has been successful or not.

To secure exposure which have been brought under control, continuously stays under control, monitoring exposure of the population can be done (Holst *et al.*, 2002).

2.1.1. Decision rules

To decide whether exposure in the working environment is below or above OEL, decision rules have to be set up. We suggest introducing a value LOC_i (Level of Concern at individual level), to decide whether exposure level is acceptable or not. Basis for decisions can be expressed as:

$$LOC_i = k \times OEL \qquad (3)$$

where LOC_i is the 'Level of Concern', OEL is Occupational Exposure Limit and k is a constant ($0 \leq k \leq 1$). Results of measurements are compared to OELs. Decision rules about LOC_i and k (Eq. 3), whether the level of exposure is too high, are depending on legislation of the country, political and economic decisions of when to act. The value of k is thus determined upon properties of the particular substance, toxicity, adverse effects and safety factor to account for measurement uncertainty etc. The time period of exposure measurement, whether short-term (<15 min.) or long-term exposure is considered, influence decisions about the value of k as well.

Exposure of a population is in control when exposure is below LOC_i. To be sure that the exposure level of almost all people exposed (e.g. 95%) are sufficiently below OEL, k is fixed depending on two parameters: the location of the geometric mean (GM) and the variability of the exposure distribution. In the present paper, the scope of protecting the worker against being exposed above the OEL has changed towards controlling the compliance of OELs. It is assumed in this paper, that the worker can be protected by proper choices of OELs and k.

2.1.2. Concluding remarks

Due to economic reasons, it is proposed to pre-screen the lines of industries in 'good' and 'bad' at the overall level. Accordingly mapping is done to locate the problem to identify exactly which companies to investigate (the 'bad' ones). Mapping can be done partly on the basis of previously obtained data and on results obtained from few new measurements. Exposure assessment at the individual level can now be done. It is of great importance to choose a proper measurement strategy to obtain reliable results.

When the 'problem' has been identified, located and quantified, the next step is intervention if needed to solve the 'problem'. Substitution of a compound or improving ventilation at the workplace, are examples of possible interventions. The purpose is to reduce or eliminate exposure

of workers to the contaminant. After the intervention it is necessary to perform an exposure assessment to verify if the intervention has been successful or not. Depending on the outcome of the exposure assessment more intervention may be needed. When exposure to the contaminant has been reduced sufficiently, which means that the population's exposure is under control, monitoring is conducted to secure that exposure stays under control.

The purpose of putting up these proposals and steps to investigate exposure for a given contaminant or 'problem' in the working environment and locate 'problems' at the workplaces, is to improve the conditions at the workplaces and to get a possibility of eliminating the 'problem' at present. The steps proposed in this paper results in a preventive way of solving a 'problem' in the working environment in the future compared to the more traditional retrospective, epidemiological way of solving it after serious illness or death has appeared.

The concentration of a given substance in the breathing zone of an exposed person is varying within the working day, between days and between years. Usually a working day is a suitable unit of time, which is appropriate for measurements used for compliance.

It is the arithmetic mean (AM) of a concentration during an even longer exposure period, which is connected to the risk of adverse health effects due to long-term exposure of a single worker (Rappaport, 1991).

2.2. Considerations on variability in exposure

There is a large variability in the exposure level from day to day at workplaces within and between different lines of industry, different companies, departments and persons. It is important to be aware of the variability connected to the measurements in the working environment. Variability can be illustrated by a hierarchical catalogue of exposure distributions. It is important to note that the object of measurement is not a single value, but a distribution. Figure 2 shows the different sources of variation to consider when estimating exposure for a hazard, which could be a given substance at the workplace, mix of substances e.g. mineral spirit or mineral dust. The six 'upper' boxes describes a 'natural' variation or variation of the object itself. The last box describes uncertainty due to measuring exposures.

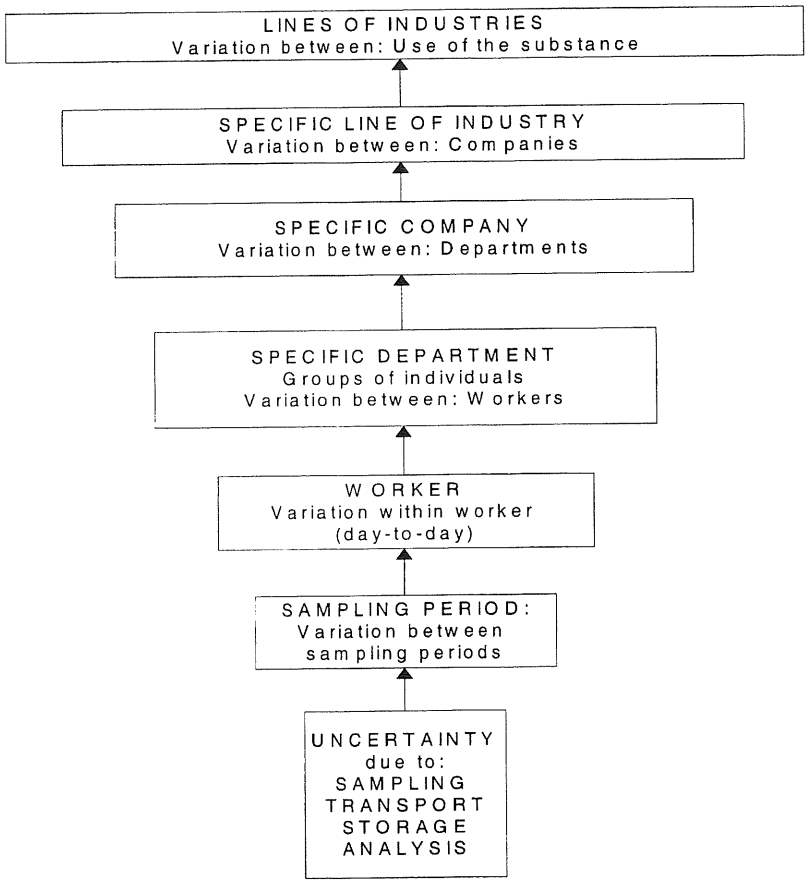

Figure 2. Exposure for a given substance at the workplace. Variability connected to the exposure level. A hierarchical catalogue of distributions.

Even in an ideal situation in which perfect measurements of all persons were obtained, the differences illustrated in Figure 2 will exist. For instance when assessing a persons' exposure for a given substance, the question raised is not: 'What is the exposure?' but rather: 'What is the mean exposure over a period?' or 'Between which values do we find 95% of the daily exposures?'. For a group of workers in a given industry, exposed for a given agent, it has been observed that there is a factor of 20-30 between the lowest and highest measurement (Kromhout *et al.*, 1993). The last box in the hierarchical catalogue of variations shown in figure 2, includes the uncertainty due to sampling, transport, storage and analysis, which are all uncertainties that ought to be considered, when measurements of exposures in the occupational environment are done.

The variation in the last box in Figure 2 is expected to be approximately normal distributed. Uncertainty due to analysis etc. is expected to be symmetrically and small with a narrow peak. Day to day variation in exposure and variation during the day for a person are expected to be normal distributed as well, but with a more broad profile. It has been observed that measurements of process concentrations for a given process performed by different persons are approximately normal distributed (Nyeland *et al.*, 2002; Olsen, 1994).

2.3. Exposure and emission

As described in the introduction the available exposure dose (E_{DA}) can be expressed as the product of the exposure concentration (C) or the arithmetic mean air concentration and the time period (T)

A worker's exposure concentration can be measured in two fundamentally different ways, either in the time domain or in the process domain as described below.

2.3.1. Time domain

When exposure to air pollutants of people in the occupational environment is measured, the object of measurement is the air inhaled by the worker during a working day. Traditionally it is measured in the breathing zone of the person. For logistic and economic reasons one day is a practical time unit, a time unit matching OEL. The measurand is the concentration of pollutant in the air in the breathing zone of the worker during the sampling period.

In practice, sampling periods commonly are less than 8 hours due to technical reasons. In these cases sampling is done in several consecutive periods without any consideration about the processes the worker performs during the sampling period. This kind of sampling is called sampling in time domain (Olsen, 1994). An averaged concentration of the day is calculated as the time-weighted average concentration (TWA). Results from this kind of sampling are often imbedded with a large variation. It is problematic, when exposure measurements are not attached to the operated processes.

2.3.2. Process domain

Emission from a given process of the substance considered is the primary source of worker's exposure. The working day can be divided in a series of processes. Process concentration is measured by measuring the air in the breathing zone of several operators performing a given process. A process concentration (**PC**) is estimated by averaging several measurements on the same process performed by different operators. These measurements are usually symmetrical distributed even when the process is operated by different persons (Olsen, 1994). Due to the quality of the product the working procedure are often carried out equally. Sampling time for process measurements is much shorter (about 15 minutes) compared to sampling time for day measurements.

2.3.3. Exposure distributions (log normal)

In exposure assessment the relevant measure of exposure is the true AM of the exposure concentration during the exposure period, because risk is proportional to AM (Rappaport, 1991). Due to the fact, that exposure and thus AM of the exposure of a person in the working environment differs from day to day during a whole year, it is important to investigate how AM is distributed during a whole year. It has been shown, that data on shift-long exposure concentrations of a worker for chemical substances in the working environment is log normal distributed during a year (Esmen *et al.*, 1977; Kromhout *et al.*, 1993; Rappaport, 1991). The parameters of the lognormal distribution are the logarithm of the geometric mean (GM) (the value of the median (50%-quantile)) and the logarithm of the geometric standard Deviation (GSD). GM is often used as a measure of exposure concentration in the literature. GM cannot be interpreted physically. But for data that are log normal distributed GM may be a better estimate of 'the true' AM, than the AM calculated from the measured data. This is more pronounced for small data sets, in which AM is more sensitive to a few data points from the upper part of the lognormal distribution tail.

A property of the lognormal distribution is, that the value of the median (50%-quantile) (GM) is lower than the arithmetic mean value. The probability of obtaining a value below the arithmetic mean is thus much larger than the possibility of obtaining a value above the arithmetic mean when performing a single measurement. It is thus not sufficient to sample once at each worker. To describe the exposure distribution sufficiently it is necessary to perform several measurements, to obtain an estimate of the spread, to avoid underestimation of the exposure. It is reported, that the uncertainty due to day-to-day variation within worker of the exposure often is larger than the between worker variation (Kromhout *et al.*, 1993; Rappaport *et al.*, 1993; Rappaport *et al.*, 1995).

All in all it is of great importance to investigate how the Arithmetic Means (AM) for exposure of each worker in a population are distributed to estimate the distributions. It is important to collect enough data on exposure (from measurements, from exposure models etc.) to obtain sufficient statistical power to discriminate exposure between workers, to discriminate exposure before and after intervention or to decide whether OEL has been exceeded or not.

The purpose of bringing the individual exposure distributions under control, as suggested in this paper, is to change the exposure distributions to have a more narrow maximum profile with a value well below LOC_i and only few values above LOC_i (Figure 3).

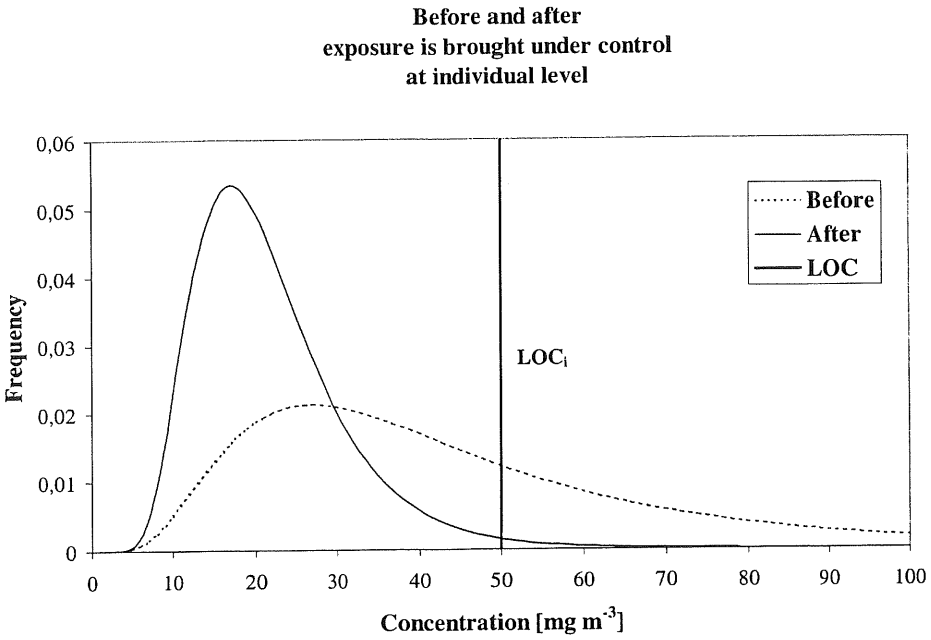

Figure 3. Distributions of the average exposure during a year, at individual level before and after exposure is under control.

3. METHODS

A proposal for more detailed steps of bringing the exposure of a population under control is illustrated by a flow diagram (Figure 4), going from the pre-initial step 'Information' (hazard evaluation) and the initial step 'Mapping' to the step 'Population Monitoring'. These general steps for conducting an exposure assessment are in agreement with the guidelines outlined in the CEN standard (European Commitee for Standardization (CEN), 1995).

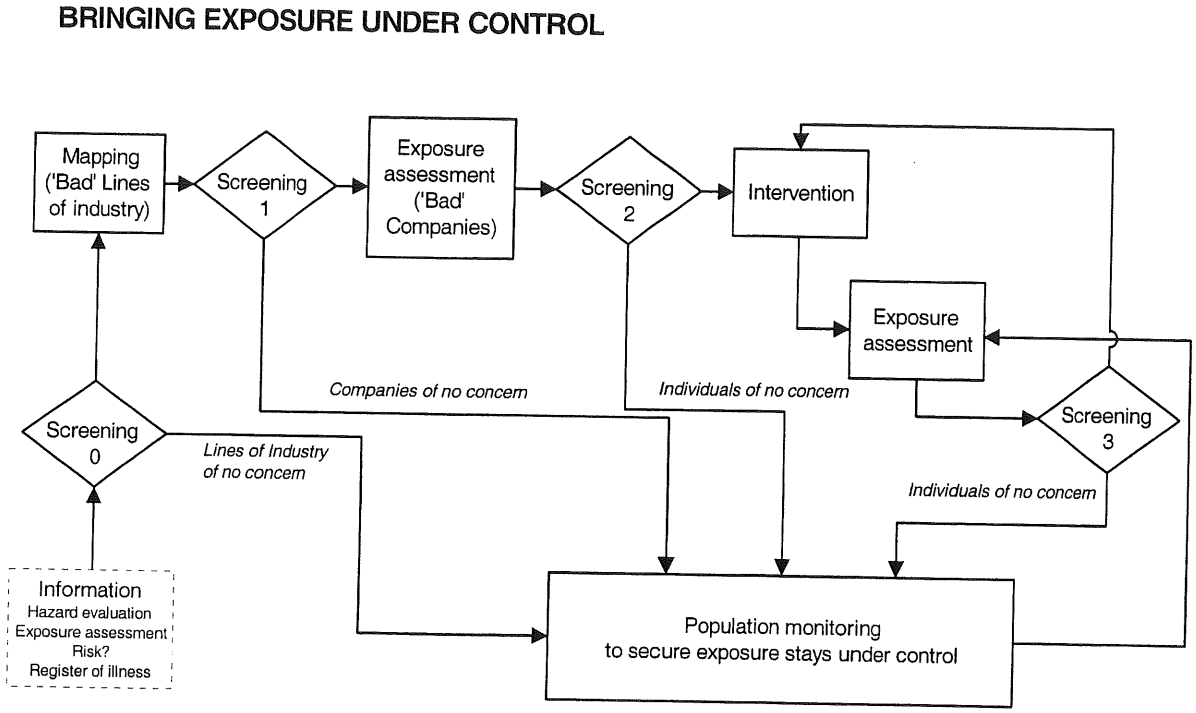

Figure 4 shows the steps in bringing the exposure under control of a population of objects from the occupational environment: Information, Screening 0, Mapping, Screening 1, Exposure Assessment, Screening 2, Intervention, Exposure Assessment, Screening 3 and at last Population Monitoring to secure that exposure stays under control.

Steps of bringing exposure under control (Figure 4)

3.1. Information and Screening 0

To trace and define the 'problem' or the hazard to investigate, information can be obtained in e.g. a register of illness. The pre-initial step is to gather all information available on the substance investigated to evaluate the risk. This is done by performing a hazard evaluation and exposure assessment by collecting information in the literature and from available sources to form the base for evaluating the risk.

A way to estimate exposure for epidemiological use is by the use of job titles or occupational titles assuming that these represent a specific exposure profile for each job group. This way of estimating exposure is very coarse. Workers having the same job title may not be exposed to the same level of exposure as well as for the same kinds of agents (Stewart *et al.*, 1986). A more specific method is by using 'job-exposure-matrices' where a job/industry-axis (input) and an exposure-axis (output) are used. The matrix generates specific exposures of a worker in a certain job (Gerin *et al.*, 1985).

3.2. Mapping and Screening 1

Mapping is the first move to make when monitoring exposure of the populations in the different lines of industries in the working environment. Mapping is done to get a coarse picture of the population's exposure and can be used for a first division of industries in those being acceptable and those not. This can be done in various ways e.g. by linking information from databases on compositions of the products used in different lines of industry, by observations at random sample of facilities or from historical data on exposure or by measurements at the workplace. Based on this result screening out the lines of industry according to high/low exposure level can be done.
Involuntary, groups of people will be classified incorrectly (Figure 5).
This information forms the base of screening out the lines of industry being highly exposed.

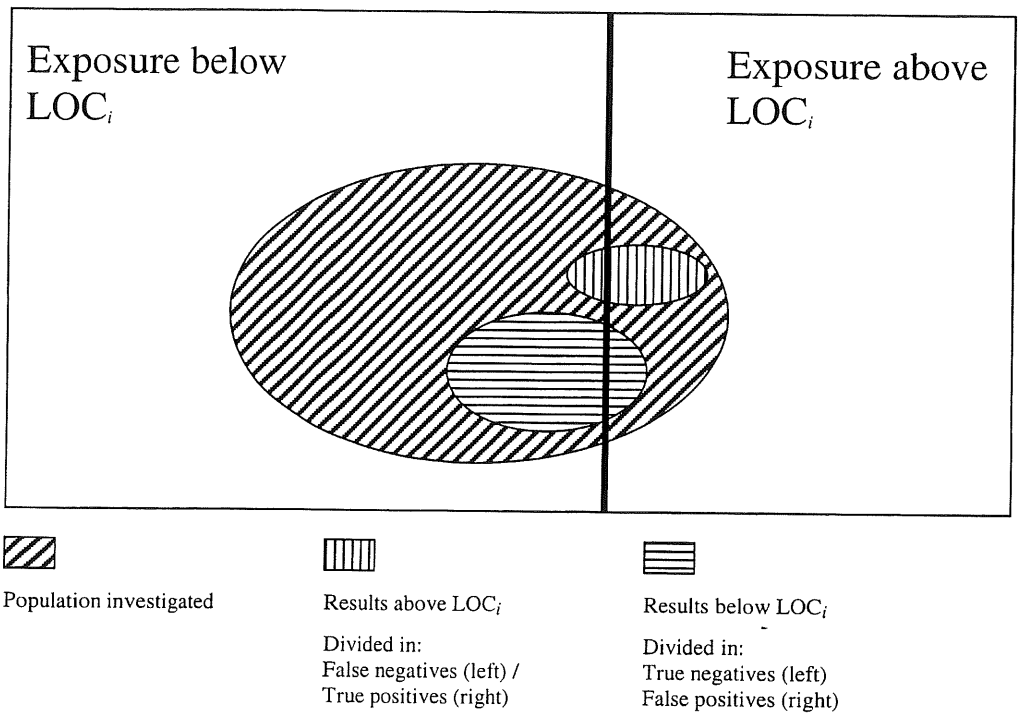

Figure 5 - Illustration of the exposure of a population.

The big rectangle is the whole population, divided in a group with exposure below LOC_i and a group with exposure above LOC_i. Exactly where the line goes is obviously unknown. The population selected after screening 0 is shown inside the big oval. Results with exposure above LOC_i is pictured in the small oval and results with exposure below LOC_i is pictured in the medium sized oval.
Two groups of people are placed with 'incorrect' labels. Those being false negative (with results above LOC_i, belonging to the group exposed below LOC_i) and false positive (with results below LOC_i, belonging to the group exposed above LOC_i).

Various methods exist which differ in cost and accuracy. A qualitative picture can be obtained by linking information from the VAT section of the Danish Bureau of Statistics with information from the database PROBAS (The 'Product Register', Denmark), a national register of chemical substances and commercial products containing information of the composition of the products produced in or imported to Denmark. Information from these databases form the basis for selection of a study group for further investigation. This is a cheap but coarse method.

Quantitative estimations of exposure can be carried out using historical data. Historical exposure data however are often biased and of poor quality. It is for instance of great importance to check if data are comparable before merging data generated under different sampling strategies (Olsen *et al.*, 1991). A strict classification into homogeneous groups has to be established and enforced to avoid introduction of considerable bias due to the different strategies used.

There are several other ways for mapping and screening to get more quantitative data on exposure levels. One way is to visit at random sample of facilities, to observe working conditions at the workplace: Working patterns, processes, materials and products, localisation of exposure sources, job, ventilation, etc. From observations it is possible by the use of e.g. the program EASE (developed by Health and Safety Executive (HSE), Great Britain) to calculate and estimate exposure levels or the program EUSES (based on the EU Technical Guidance Documents) a decision-support system for the evaluation of the risks of substances to man and the environment (EUSES – the European Union System for the Evaluation of Substances).

Measurements can also form the basis for a quantitative mapping and screening. Usually these measurements are only carried out once at each worker. Often decisions about where to sample (at which processes and which persons) are only made by observations, without any pre measurements. Several studies have shown, that it is very difficult to make these decisions this way. Incorrect choices are made resulting in erroneous measurements (Hawkins *et al.*, 1989; Kromhout *et al.*, 1987; Post *et al.*, 1991; Woitowitz *et al.*, 1970).
Measurements are done to find 'black spots' where exposure exceeds LOC_i.
Traditional practise of testing 'compliance' with occupational exposure limits (OEL's) should be avoided. Instead exposure should be defined with reference to the exposure distribution.

Another way to map is to measure twice at each person followed by calculation and estimation of exposure levels using nested mixed effects models (Rappaport *et al.*, 1999).

Mapping and screening grouped by industries should be done with care. The line of industries should be subdivided in different groups according to different kinds of work because of large exposure variability (e.g. the graphic line of industry in Denmark can be subdivided into groups as for instance: Heatset printing, Silk printing etc.).

3.3. Exposure assessment and Screening 2

From the lines of industries with exposure above LOC_i a random sample of companies is selected. In each company a random sample of people is selected.

The objective is to collect enough exposure data for each randomly selected person to render sufficient statistical power to discriminate between the people, which are truly exposed above OEL and those not. This can be done, by choosing one of several measurement strategies. Exposure assessment of individuals can also be used for decisions about intervention.

Method

The method for exposure assessment can be divided in the following 3 steps:

1. **Random selection of companies** with exposure > LOC_i from the lines of industry.
   Usually done by the same procedures as described in 'Mapping and screening 1'.

2. **Selection of exposed people** randomly within the company.
   Usually done by the procedures described in 'Mapping and screening 1'.

3. **Measurement Strategies**

3a. Measure enough days to obtain an accurate picture of the exposure distributions.
This method for air measurements is usually done by the use of pumps. Air is drawn through a filter, where particles/compounds are caught. An occupational hygienist has to be presented during the sampling period.

3b. Strategy 1: 'Measured 8h-TWA Strategy', measured by self-assessment exposure (SAE) (Rappaport *et al.*, 1999). A passive sampler is used for this sampling method, containing material where compounds are adsorbed. This method can be administered by the workers themselves (Liljelind *et al.*, 2000). Data are analysed by mixed model procedure. Variance within and between worker can be estimated. The exposure model is set up in section 6. Appendix.

3c. Strategy 2: The logbook method and process measurements

The logbook method (Olsen, 1994) is another way to get a more complex picture of exposure at individual level and to catch 'black spots'. Exposure intensity and duration are measured independently. The time spent at each process (start and stop) are recorded by the worker in a logbook in a period of e.g. 15 working-days and the concentration of each process performed during the working day is measured. An exposure matrix of each worker for each measurement day can be established based on **PC** (C) and logbooks (T).

Using the logbook method individual exposure levels can be estimated, short-term as well as long-term exposure. Day-to-day variation can be estimated. Costs for measuring can be reduced by measuring the process and background concentrations only a few days. Some process concentrations can be modelled.

Startegy 3: The WSS-logbook measurement method

The logbook method can be combined with SAE or WSS to estimate process concentrations. Applying this strategy, work pattern (time spent at the processes) should preferably be such that the columns in the logbook-matrix are linearly independent. Otherwise it is not possible to obtain reliable estimates for **PC**s. Individual exposure levels can be estimated (short- and long-term exposure) as well as day-to-day variation. The obtained, estimated values for process concentration can be used for further estimation of long-term exposures for workers using the logbook method, reducing the need for WSS-measurements.

When process concentrations are estimated, it is possible by using the logbook methods to estimate exposure in an even larger scale, based on logbooks and estimated process concentrations, without conducting any further air measurements. It is even possible to estimate exposures of workers at individual level, prospectively based on expected time intervals spent at each process.

3.4. Intervention

When the exposure level is too high it can be necessary to intervene by ventilation, changing the product, changing the working pattern etc. The aim of interventions is to lower the exposure below LOC_i.

Data obtained by measurement strategy 3c can be used as a quantitative base for decisions about intervention (changes in exhaustion, substitution of a product etc.). Data obtained by 3b can only be used for general decisions about intervention at group level. The logbook method can be used for pointing out where to possibly introduce an intervention at local level and forms a quantitative measure for where and when to intervene.

3.5. Exposure assessment (of intervention) and Screening 3

After intervention, exposure is measured in order to confirm that it is below LOC_i. In case exposure is below LOC_i, population monitoring is the next step. Otherwise a new intervention is made.

3.6. Population monitoring

If no further intervention is necessary and exposure is below LOC_i, population monitoring will be the last step for exposure monitoring prospectively (Holst *et al.*, 2002).

The objective is to monitor exposure of a population in the occupational environment, brought in control by the steps previously described, where no 'black spots' in the population are left. This kind of monitoring will be highly useful in occupational health work, it will result in more reliable measurements and reduce the need for measurements (economic benefit).

In case of changes in the working environment at the company, resulting in increased exposure level, a risk reassessment has to be redone. This will maybe require new measurements at the individual level and/or interventions.

4. DISCUSSION

A central task, when performing exposure assessment, is the choice of an appropriate measurement strategy. It is important to be aware of the objective of performing the exposure assessment. Considerations on reliability of the measurements, e.g. whether they are bias-free or not as well as economic considerations are important factors. Four kinds of measurement strategies have been outlined in the section 3.3. Three of these are strategies implemented and have all previously been used for exposure assessment in the occupational environment, the forth is proposed in this script. Pros and cons of these strategies are interesting to discuss in connection with exposure assessment and bringing exposure under control.

The first method described (3a) - measure enough days to obtain an accurate picture of the exposure distribution - is the most reliable strategy, but the most unrealistic due to practical and economic reasons. A reduced form of this measurement strategy is the 'Worst Case' strategy (EN 689, (European Commitee for Standardization (CEN), 1995)), in which the occupational hygienist during inspection chooses the worst cases by observation and only measures these selected ones. It is a practical strategy without any theoretical base. This strategy is not recommended, when the aim of the exposure assessment is to get a description of the actual exposure distribution. Measurements are biased towards higher values, when using this measurement strategy (Olsen *et al.*, 1991). Further it has been shown that expert judgement is not reliable (Hawkins *et al.*, 1989; Kromhout *et al.*, 1987; Post *et al.*, 1991).

The second method described (3b) is one proposed by Rappaport (random sampling, SAE, data analysed by using random effects model or mixed model). The object of measurement is the exposure of a population of workers and the measurand is the populations or subpopulations distribution of individual arithmetic mean concentrations. When using this strategy it is thus not possible to estimate the arithmetic mean exposure concentration for the individual worker. The strategy is suitable for epidemiological studies. Intervention at the population level is possible e.g. by introducing general ventilation or substitution of dangerous substances with less harmful ones.

The logbook method (3c) provides data to assess the exposure of each individual worker, to be used for bringing exposure under control as suggested by this script. Under this measurement strategy it is possible to intervene at a more specific and local level. Data obtained provides information to identify processes contributing most to the total exposure and process environment, information to be used directly for improvements of the workplace. Data provides a base for priority

in decision-making on how, where and when to intervene. 'Worst case' measurements will be included in the data material sampled using the logbook method in a well-defined form. Data are suitable for exposure modelling and it is possible to establish a working process/exposure-matrix too, which will make it possible to reduce the need for measurements, prospectively. At a first glance the logbook method looks more expensive than the more traditional exposure measurement strategies (where only measuring one or a few days). Prospectively it will reduce the costs, due to the reduced need for measurements.

The WSS-Logbook measurement method, described and proposed in this script, is a variation of the logbook method. Sampling is based on WSS (aggregated, 8 hr, concentration measurements, which can be sampled by workers themselves) in combination with logbook keeping (time estimates). The need for an occupational hygienist present during the sampling period is eliminated. Data are analysed using general linear models in which it is possible to estimate process concentrations. Short- and long-term exposure can be estimated as well as day-to-day variation. To obtain reliable estimates for process concentrations, large amounts of data are needed. The WSS-Logbook measurement strategy will thus be suitable for large studies and studies in which work pattern (time spent at the processes) are preferably such that the columns in the logbook-matrix are linearly independent. Otherwise it will not be possible to obtain reliable estimates for process concentrations. Uncertainty on the exposure estimates, using this measurement strategy are expected to be larger than the uncertainty using the logbook method, but more accurate than the estimates obtained by the 'Measured 8h-TWA strategy'. The WSS-Logbook method is useful for exposure assessment at the individual level. When implementing an exposure model based on exposure data from another company it is necessary to validate the model, based on new measurements.

5. CONCLUSIONS

For exposure assessment at the individual level, as illustrated in Figure 4 on bringing exposure under control before monitoring prospectively, measurement strategies such as the logbook method or the WSS-logbook method are suitable. These methods provide quantitative data on different processes contributions to workers exposures. Such information can be used for decision making on improvement of the working environment. Depending on the size of the population investigated it is decided which strategy to choose. The logbook method is suitable for both smaller and larger populations. Applying the WSS-logbook strategy, work pattern (time spent at different processes) should preferably be such that the columns in the logbook-matrix are linearly independent to obtain reliable estimates for **PC**. The WSS-Logbook Strategy is suitable for larger populations and it is appropriate to be used as a screening method.

6. APPENDIX

Measurement Strategy 3b.

Strategy 1: 'Measured 8h-TWA strategy', measured by self-assessment exposure (SAE) (Rappaport *et al.*, 1995; Rappaport *et al.*, 1999).

MODEL 1: $Y_{h(ij)} = ln(X_{h(ij)}) = \mu_y + \alpha_h + \beta_{h(i)} + \varepsilon_{h(ij)}$

MODEL 2: $Y_{h(ij)} = ln(X_{h(ij)}) = \mu_y + \alpha_h + \sum \delta_m C_{mh(ij)} + \beta_{h(i)} + \varepsilon_{h(ij)}$

$X_{h(ij)}$	-	Exposure level on the j-th day for the i-th worker in the h-th job
μ_y	-	The underlying, mean exposure level over all jobs
α_h	-	The fixed effect of the h-th job $\quad \Sigma\, \alpha_h=0$
$\sum \delta_m C_{mh(ij)}$	-	Additional fixed effects for task- and process-related covariates (m=1,2,3....p) where the regression coefficients $\delta_1,\delta_2,\delta_3 \ldots \delta_p$ represents the fixed effects of the p covariates
$\beta_{h(i)}$	-	The random effect of the i-th worker $\quad$ (~iid; $N(0,\sigma^2_{B,h})$
$\varepsilon_{h(ij)}$	-	The random effect of the j-th day for the i-th worker $\quad$ (~iid; $N(0,\sigma^2_{W,h})$

Model 1 is a simple model in which the only deterministic variable is the job titles of the worker. Within and between worker variance are estimated. Model 2 is a model in which additional fixed effects from task- and process related covariates are included. Data from measurements are log transformed i.e. exposure is assumed to be lognormal distributed. Effects in the model are assumed to act multiplicatively on exposure level due to that it is exposure of the group that is modelled.

Measurement Strategy 3c.1.

Strategy 2: The logbook method and process measurements.

The following matrix of each worker can be established:

MODEL:

$$C_{Day1} = f_{P1,\,Day1}\, PC_{P1} + f_{P2,\,Day1}\, PC_{P2} + \ldots.$$

$$C_{Day2} = f_{P1,\,Day2}\, PC_{P1} + f_{P2,\,Day2}\, PC_{P2} + \ldots.$$

.....

$$C_{Dayi} = f_{P1,\,Dayi}\, PC_{P1} + f_{P2,\,Dayi}\, PC_{P2} + \ldots.$$

$C_{Day\,i}$ - the time-weighed average (TWA) concentration of pollutant during working day i.

$f_{Pj,Day\,i}$ - the fraction of day i, during which process j is performed.

PC_{Pj} - the process concentration (**PC**) of the j'th process.

The process concentration (**PC**) is calculated as:

$$PC = \bar{C}_{Pj} = \frac{1}{N}\sum_{n=1}^{N} C_{Pj\,n}$$

P_j - process j

N - number of measurements

n = index

Measurement Strategy 3c.2.

Strategy 3: The WSS-logbook measurement strategy.

The matrix shown under Strategy 2 is solved, for unknown PC_i values, based on 8h TWA measurements (C_{dayi}) and time measurements from logbooks ($f_{pj,Day\,i}$) as a general linear model (applying PROC GLM, SAS statistical software).

MODEL: $$X_{h(ij)} = \mu_y + \alpha_h + \sum_{m=1}^{m=p} f_m C_{mh(ij)} + \beta_{h(i)} + \varepsilon_{h(ij)}$$

$X_{h(ij)}$ - Exposure level on the j-th day for the i-th worker in the h-th job

μ_y - The underlying, mean exposure level over all jobs

α_h - The fixed effect of the h-th job or department $\Sigma\,\alpha_h=0$

$\sum_{m=1}^{m=p} f_m C_{mh(ij)}$ - Where the regression coefficient f_m (the fraction of time spent at p processes during a working day), represents the fixed effects of the covariates, C_m, (m=1,2,3...p) (the processes performed) on the j-th day, based on the logbook filled in by the i-th worker.

$\beta_{h(i)}$ - The random effect of the i-th worker (~iid; N $(0,\sigma^2_{B,h})$

$\varepsilon_{h(ij)}$ - The random effect of the j-th day for the i-th worker (~iid; N $(0,\sigma^2_{W,h})$

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Paper [F]

MONITORING A POPULATION OF EMPLOYEES FROM THE OCCUPATIONAL ENVIRONMENT

[F] MONITORING A POPULATION OF EMPLOYEES FROM THE OCCUPATIONAL ENVIRONMENT

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Summary

The paper outlines methods to monitor a population of employees who are exposed to a hazardous volatile compound. It is assumed that the daily exposure characterising an individual employee is fluctuating randomly in time. Each employee is thus characterised by a statistical distribution of the so-called *Time-weighted average concentration* (TWA), and the distribution characterising the population is a compound distribution of the individual distributions. In general the compound distribution characterising the population will not be a standard distribution. It is reasoned that the compound distribution in some cases can be approximated by a log normal distribution. For any employee the TWA value should never exceed a limiting value, LV. Relevant population parameters are monitored by sampling in order to observe whether the conditions in the population should give rise to any concern. The parameters chosen are the probability, p, that a randomly selected employee has a TWA value exceeding LV together with the mean of the TWA values in the population. Relations between the criteria for these parameters have been calculated. Under the assumption of log normal distribution statistical tests have been developed for testing whether p and the mean in the compound distribution are exceeding limits of concern. Confidence intervals for p and the mean are provided.

Keywords: Environmental monitoring; limiting value; compound distribution; log normal distribution; test for mean; test for exceeding a limiting value.

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1. Introduction

Consider an employee exposed to a hazardous compound during the working day due to the work with one or more processes. The dose of the compound received after the working day is primarily dependent on the exposure from the processes and on the time performing the individual processes. In general it cannot be expected that working environment is the same for the employee during the year. The dose received of a specific compound will therefore not be constant from day to day. The daily dose received should therefore be expressed in form of a time series. When the time series can be assumed to be stationary, then a distribution of the dose received on a randomly selected day exists. The individual employee can therefore be characterised by a density function for the daily dose received. For many volatile compounds there exist requirements for the size of the dose received by the individual employees. For volatile compounds the requirements are normally given in form of a limiting value, LV, expressed as a maximum for the average concentration the employee is exposed to during the working day. This concentration is denoted the *Time-weighted average concentration* (TWA).

Consider a specific volatile compound and assume that each employee in a population can be characterised by a density function for their TWA. The distributions in a random sample of employees from the population could then result in the sample displayed in Figure 1a. In case the limiting value for the TWA is e.g. 9 mg/m^3, it is obvious that the population must contain many "black spots" i.e. employees for whom TWA exceeds LV for relatively many working days. The individual employees in the population should therefore be monitored individually in order to change the environment in such a way that the distributions are "moved" to the left (e.g. by introducing new technology for the processes performed by the employees).

However, when a population of employees has been monitored at the individual level for some years most "black spots" may have been nearly eliminated. The distributions in a random sample of employees from the population could then be displayed as shown in Figure 1b. Figure 2 displays the procedure for bringing exposure in control. Nyeland et al (2002) have proposed this procedure in agreement with the general steps of performing an occupational exposure assessment (CEN, EN 689, 1995). Since the population now can be considered as reasonably homogenous with most employees satisfying the requirements for the TWA, the strategy of monitoring should then be changed. The focus should now primarily be on the population instead of the individual employees. The purpose of the population monitoring is to ensure that the values of the TWA for the employees in the population have not increased e.g. due to changes in the state of the technology applied, to changes in the educational level of the employees etc. The assurance is obtained by the

monitoring of relevant population parameters. Therefore, the criteria for performing a population monitoring would normally include defining "limits of concern" (LOC) for the values of some of the population parameters. It should be observed that the LOC values are defined for the parameters in a population and not for the individual employees.

A number of problems are connected with the monitoring of a population of employees from the occupational environment. It is not always obvious which population parameters should be monitored. It is necessary to determine the relation between the relevant parameters defined on the individual employees in the population and the parameters in the distribution of measurements on employees sampled from the population. Normally, the mean, the median or another quantile (e.g. the 0.95 quantile) in the distribution are monitored (Armstrong, 1992; Rappaport and Selvin, 1987, Rappaport 1991).

The purpose of this paper is to outline the problems of the monitoring of a population of employees and to provide statistical tests for testing whether the parameter values have exceeded limits of concern.

2. The purpose, strategy and tactics for monitoring a population of employees.

Consider a population of employees. Each of the individual employees in the population is characterised by a distribution of TWA values for the volatile compound. The limiting value for the TWA values is denoted LV.

Before starting the process described in Figure 2 many of the distributions of the TWA values in the population could be expected to have large probabilities for exceeding LV (see Figure 1a).

The purpose of starting the process described in Figure 2 is to bring the exposure in control i.e. reducing the probability of individuals in the population having TWA values exceeding LV (see Figure 1b). Assume that this state has been achieved and it has been decided to start a monitoring of the population (see Figure 2).

As an ideal, the TWA value should not at any time exceed LV for any of the employees in the population. In the ideal situation the probability should thus at any time be zero for an employee having a value of the TWA exceeding the limiting value. However, this cannot in general be expected to be the case. It can be expected that a number of employees will occasionally have inadmissible values of the TWA. Therefore, the purpose of the population monitoring should be to minimise the relative number of employees, which have positive probabilities of having a TWA value exceeding LV. As the values of the TWA for the individual employees fluctuate randomly in time, a monitoring programme can only obtain this objective indirectly. In a monitoring programme

it is only possible to monitor whether the limits of concern defined for the parameters in the distribution of TWA values have been exceeded.

In the strategy for the monitoring it must then be tolerated that a small fraction of TWA values in the population at any time will exceed LV. For some compounds this would be tolerable when it can be assumed that an individual employee only occasionally has a TWA value exceeding LV. Depending on how hazardous the compound is, the size of this fraction should be pre-set.

In the first place the tactics for the monitoring should be to define the population parameter or parameters, which have to be monitored according to the strategy chosen. Then a statistical procedure should be constructed in such a way that there exists a high probability for telling whether the values of parameters monitored exceed or do not exceed limits of concern.

3. The mathematical model

Let Ω denote a population of N employees where the individual employee is characterised by the TWA value from the volatile compound. For each employee, the value of the TWA varies stationary in time, and each employee is thus characterised by the density function of the values of the TWA. For employee No. i the TWA is characterised by the continuous random variable X_i, which has the density function $f_i(x)$ (i = 1, 2,..., N). In general, it would be convenient to assume $a_i \leq X_i \leq b_i$, where $0 \leq a_i < b_i$. The probability that the value of X_i at any time has a value less than or equal to x is $P(X_i \leq x) = F_i(x)$, where $F_i(x)$ is the distribution function of X_i.

For a measurement of employee No. i we have: $a_i \leq X_i \leq b_i$ (i = 1, ..., N).

When $f_i(x)$ has only one local maximum i.e. is unimodal, it is reasonable for practical purposes to describe the distribution of X_i with a generalised Beta-distribution. The distributions in Figure 1a and b are all generalised Beta distributions. The density function for this distribution is:

$$f_i(x) = \frac{\Gamma(r_i + s_i)}{\Gamma(r_i)\Gamma(s_i)}(b_i - a_i)^{(1 - r_i - s_i)}(x - a_i)^{(r_i - 1)}(b_i - x)^{(s_i - 1)} \qquad (1)$$

where $a_i \leq x \leq b_i$; $r_i > 0$; $s_i > 0$ and $0 \leq a_i < b_i$.

Ideally, no value of b_i should exceed LV i.e. we should have $b_i \leq LV$ (i = 1, 2, ..., N). If this can be assumed to be almost true a monitoring of the population should be started according to Figure 2.

The probability of employee No. i having a TWA value exceeding LV is

$$p_i = \int_{LV}^{b_i} f_i(x)dx \qquad (2)$$

When $LV \geq b_i$ then $p_i = 0$. Let W_t denote the number of employees in the population with TWA values exceeding LV at the time t. In general the individual probabilities $(p_1, p_2, \ldots, p_N)$ will not be identical and the distribution of W_t will not be a binomial distribution. The probability distribution of W_t is complicated and only the mean, $E(W_t)$, and the variance, $Var(W_t)$, of W_t are normally of interest. Box et al (1978) give the following values for $E(W_t)$ and $Var(W_t)$:

$$E(W_t) = N\mu_p \text{ and } Var(W_t) = N\mu_p(1 - \mu_p) - N\sigma_p^2 \tag{3}$$

where μ_p is the arithmetic mean of $(p_1, \ldots, p_N)$ and σ_p^2 is the variance between the individual probabilities. Inserting $\sigma_p^2 = \sum_{i=1}^{N}(p_i - \mu_p)^2/N = \sum_{i=1}^{N}\frac{p_i^2}{N} - \mu_p^2$ in the expression for $Var(W_t)$ in equation (3) we obtain

$$Var(W_t) = N\mu_p - \sum_{i=1}^{N} p_i^2 \tag{4}$$

From equation (3) and (4) it is obvious that in order to reduce the size of W_t the size of μ_p should be reduced.

Consider now a random experiment where an employee is selected randomly from Ω. Let the random variable X be the TWA for the employee sampled. We then have $a \leq X \leq b$, where $a = \min(a_i)$ and $b = \max(b_i)$; $(i = 1, 2, \ldots, N)$. As all the employees have the probability 1/N of being selected, the density function of X is

$$g(x) = \sum_{i=1}^{N} f_i(x)/N \tag{5}$$

The population of employees is thus characterised by the compound distribution g(x).

From equation (5) it is seen that the distribution of X depends on the distribution of X_i $(i = 1, 2, \ldots, N)$ and on the number of employees in Ω.

The mean, E(X) and the variance, Var(X) of X are given by the following equations:

$$E(X) = \int_0^{\infty} x g(x)dx = \sum_{i=1}^{N}\int_0^{\infty} x f_i(x)dx / N = \sum_{i=1}^{N} E(X_i)/N = \mu \tag{6}$$

and

$$Var(X) = E(X^2) - \{E(X)\}^2 = \sum_{i=1}^{N} E(X_i^2)/N - \mu^2 = \sum_{i=1}^{N}[Var(X_i) + \{E(X_i)\}^2]/N - \mu^2 =$$

$$\sum_{i=1}^{N} Var(X_i)/N + \sum_{i=1}^{N}\{E(X_i) - \mu\}^2/N = \sigma_W^2 + \sigma_B^2 = \sigma^2 \tag{7}$$

It should be noted that in equation (6) and (7) μ is the weighted mean of the individual TWA means and σ_W^2 is the weighted mean of all the individual variances within employees while σ_B^2 is the variance between the individual means.

Let P(X > LV) denote the probability that a measurement of a randomly selected employee from Ω exceeds the limiting value. We have

$$P(X > LV) = \int_{LV}^{b} g(x)dx = \int_{LV}^{b} \sum_{i=1}^{N} f_i(x)dx / N = \sum_{i=1}^{N} \int_{LV}^{b_i} f_i(x)dx / N = \sum_{i=1}^{N} \frac{p_i}{N} = p \qquad (8)$$

Thus, p is the weighted mean of the individual probabilities of a TWA value exceeding LV. As the weights all are equal to 1/N p is identical to μ_p/N, where μ_p is the mean of the number, W_t of employees with TWA values exceeding LV at time t (see equation (3)). With no change of the distributions in Ω the value of p is independent of time.

4. Requirements for the parameters monitored

The distribution of X cannot in general be expected to be a standard distribution. It must be emphasised that in general the same type of distribution cannot be expected for all employees in Ω. It can be shown that even if the distribution of the TWA is a Beta distribution (equation (1)) for all employees in Ω then no closed form expression for the distribution of X is available. However, sometimes it may be possible to approximate the distribution of X by a standard distribution. The actual samples from the situations displayed in Figure 1a and b are shown in Table 1. The results from the goodness of fit tests do not contradict the assumption that the lognormal distribution sometimes can be used as an approximation to the distribution of X.

Therefore, the following model for the reference distribution of X is assumed:

The distribution of X is lognormal i.e. $X \in LN(\theta_x, \tau^2)$ and $\ln X \in N(\theta_x, \tau^2)$.

The geometric mean (i.e. the median) and the geometric standard deviation of X is then $GM = e^{\theta_x}$ and $GSD = e^{\tau}$, respectively.

In order to simplify the formulas we introduce the transformation $Y = X/LV$.

$$Y \in LN\{(\theta_x - \ln LV), \tau^2\} = LN(\theta, \tau^2) \text{ i.e. } \ln Y = Z \in N(\theta, \tau^2) \qquad (9)$$

When X is lognormal distributed, the most obvious parameter in Ω to monitor is the median since the median is the mean value in the normal distribution of ln(X). However, knowledge of the median does not give any general information of the size of p (equation (8)). Therefore, the monitoring of this probability should be performed directly.

Let N_1 denote the number of employees in the population with a positive probability of TWA exceeding LV. The smallest and the largest probability for a TWA among the N_1 probabilities are denoted υ_L and υ_H, respectively. The value of p can thus be expressed in the following way:

$$N_1\upsilon_L/N \le p \le N_1\upsilon_H/N \quad (10)$$

The requirement for p can be calculated from recommendations for N_1/N and υ_H and would then be expressed as

$$p \le p_0 \quad (11)$$

where p_0 is the LOC for p.

With this model and assuming $p_0 \le 0.5$ it can be shown that the admissible values of θ and τ corresponding to the requirement in equation (11) are located in the fourth quadrant in the (τ, θ) plane below the line

$$\theta = -u_{1-p_0}\tau \quad (12)$$

where u_{1-p_0} is the $(1 - p_0)$ quantile in the standard normal distribution.

Depending on the compound monitored it may also be important that the mean value, E(X) is less than a pre-set value which could be expressed as a fraction of LV. The requirement for E(X) would then be

$$E(X) \le \mu_0 = c_1 LV \quad (13)$$

where $0 < c_1 \le 1$ and c_1LV is the LOC for E(X). The requirement in equation (13) is important in the cases where the average of the TWA in Ω is more important than occasional exceeding of the limiting value for a few employees. However, it may sometimes be necessary to combine the requirements in equation (11) and (13).

According to equation (9) the requirements in equation (11) and (13) are equivalent to the requirements $P(Y > 1) \le p_0$ and $E(Y) \le c_1$, respectively.

The values of θ and τ satisfying the requirement in equation (13) are located in the fourth quadrant below the parabola

$$\theta = -\tau^2/2 + \ln(c_1) \quad (14)$$

The admissible values of θ and τ for the two sets of requirements are illustrated in Figure 3.

It can be shown that the line $\theta = -u_{1-p}\tau$ intersects the parabola $\theta = -\tau^2/2 + \ln(c_1)$ for

$$\tau = u_{1-p} \pm \sqrt{u_{1-p}^2 + 2\ln(c_1)} \quad (15)$$

From equation (14) it is seen that intersection implies $u_{1-p}^2 + 2\ln(c_1) \ge 0$ or

$$c_1 \ge e^{-\frac{1}{2}u_{1-p}^2} \quad (16)$$

The line is tangent to the parabola when $c_1 = e^{-\frac{1}{2}u_{1-p}^2}$. For the case p = p_0 = 0.05 we obtain c_1 = 0.258.

When there is no intersection (i.e. when equation (15) is not true) the requirement in equation (13) is satisfied if the requirement given in equation (11) is satisfied. For a given value of p_0 (or c_1) the minimum value for c_1 (or the maximum value of p_0) is calculated from equation (15).

In some situations it is convenient to define requirements for the median in the distribution of X i.e. requirements for the value of e^{θ_X}. The requirement is given as

$$e^{\theta_X} \leq c_2 LV \qquad (17)$$

where $0 < c_2 \leq 1$ and c_2LV is the LOC for the median. The admissible values of θ and τ are located in the fourth quadrant below the line $\theta = \ln(c_2)$. The lines $\theta = \ln(c_2)$ and $\theta = -u_{1-p}\tau$ will always intersect (see Figure 3). Therefore, when the requirement defined for p (equation (11)) is satisfied it does not give any overall information whether the requirement defined for the median is satisfied and vice versa.

5. Statistical tests for the population parameters monitored

When performing statistical tests for one or more of the parameters in Ω it should beforehand be known if the purpose with the tests is to ensure whether the LOC values are exceeded or not exceeded. In general it cannot be answered which of the hypotheses should be tested. It depends on who has the burden of proof. Holst et al. (2001) have discussed this problem when testing for conformity. Therefore, in this paper the statistical tests are formulated for both exceeding the LOC and for not exceeding the LOC.

The execution of the two statistical tests is based on the measurement results of the TWA value for the employees in a random sample of n employees selected from Ω.

The measurement results are denoted: $(X_1, X_2, \ldots, X_n)$.

Test for the probability of X exceeding LV

When the requirements for the probability of X exceeding the limiting value is given by equation (11) the hypotheses are written as

H_{10}: $p > p_0$ and H_{11}: $p \leq p_0$ (18a)

The corresponding hypotheses when testing for not exceeding are then:

H_{10}^*: $p \leq p_0$ and H_{11}^*: $p > p_0$ (18b)

When it is reasonable to approximate the distribution of X to a lognormal distribution the tests given in equation (18a) and (18b) can be performed in the following way:

Using the transformation $Z = \ln(X/LV)$ given in equation (9), the random sample $(X_1, X_2, \ldots, X_n)$ is transformed into $(Z_1, Z_2, \ldots, Z_n)$.

The tests in equation (18a) and (18b) are thus equivalent to the tests

H_{10}: $P(Z > 0) > p_0$ vs. H_{11}: $P(Z \leq 0) \leq p_0$ (19a)

and

H_{10}^*: $P(Z \leq 0) \leq p_0$ vs. H_{11}^*: $P(Z > 0) > p_0$ (19b)

These tests are special cases of an analogous test in the normal distribution developed by Lehmann (1959).

Let $\overline{Z}$ and S^2 be defined as

$$\overline{Z} = \sum_{i=1}^{n} Z_i / n \text{ and } S^2 = \sum_{i=1}^{n} (Z_i - \overline{Z})^2 / (n-1) \quad (20)$$

$\overline{Z}$ and S^2 are the maximum likelihood estimators of θ and τ, respectively.

The test statistic for the two tests is

$$T = \frac{\overline{Z}}{S}\sqrt{n} \quad (21)$$

It can be shown (Lehmann; 1956) that the distribution of T is a non-central t-distribution with (n – 1) degrees of freedom and the non-centrality parameter $\eta = -u_{1-p}\sqrt{n}$. H_{10} is thus rejected at the α level of significance when $T < t(n-1, \eta_0)_\alpha$ where $\eta_0 = -u_{1-p_0}\sqrt{n}$. With the same level of significance H_{10}^* is rejected for $T > t(n-1, \eta_0)_{1-\alpha}$. The power of the test is briefly discussed in Appendix.

From equation (21) it is seen that a calculation of a two sided $(1 - \alpha)$ confidence $[p_L; p_H]$ interval for p cannot be performed directly. However, a general theorem (Wilks, 1963) can be used for the calculation of a confidence interval for p. Let T_{obs} denote the observed value of T. The values of p_L and p_H are solutions to the following two equations:

$$P(T \leq T_{obs}; T \in t(n-1, -u_{1-p_L}\sqrt{n}) = 1 - \alpha/2 \quad (22a)$$

$$P(T \leq T_{obs}; T \in t(n-1, -u_{1-p_H}\sqrt{n}) = \alpha/2 \quad (22b)$$

The equations are solved numerically e.g. by the trial and error method. The principal solution of equation (22a and b) is illustrated in Figure 4.

In the SAS system the two equations can be solved by using the function TNONCT: u_{p_L} = TNONCT(T_{obs},n-1,1-α/2)/$\sqrt{n}$. Then p_L = PROBNORM(u_{p_L}). The calculation of p_H is equivalent.

The confidence interval for p can be used as an alternative test statistic for testing the hypotheses given in equation (19a and b).

Test for the mean of X

Sometimes it may be convenient to perform a statistical test concerning the value of E(X). When the requirements are given in equation (13) then the hypotheses for testing whether E(X) exceeds the LOC are

H_{20}: $E(X) > c_1LV$ vs. H_{21}: $E(X) \leq c_1LV$ (23a)

The corresponding hypotheses when testing whether E(X) does not exceed the LOC are then:

H_{20}^*: $E(X) \leq c_1LV$ vs. H_{21}^*: $E(X) > c_1LV$ (23b)

The likelihood test for testing the hypotheses in equation (23a and b) is complicated. Therefore, in this case it is convenient to perform the test using a confidence interval for $\ln\{E(Y)\}$ as the test statistic.

With the notation defined above an approximate $1 - 2\alpha$ confidence interval for $\ln\{E(X/LV)\} = \ln\{E(Y)\} = \theta + \tau^2/2$ is given by:

$$\bar{Z} + \frac{S^2}{2} \pm u_{1-\alpha}\sqrt{\frac{S^2}{n} + \frac{S^4}{2(n-1)}} = \{\ln(E_L); \ln(E_H)\} \quad (24)$$

The performance of the interval has been discussed by Zhou and Gao (1997).

H_{20} is thus rejected when $\ln(E_H) < \ln(c_1)$ while H_{20}^* is rejected when $\ln(E_L) > \ln(c_1)$. In the case where $\ln(E_L) < \ln(c_1) < \ln(E_H)$ neither H_{20} nor H_{20}^* can be rejected.

When equation (24) is used as the test statistic the power of the test depends on the joint distribution of $(S, \bar{Z})$. The calculation of the power is therefore complicated and shall not be presented in this paper.

6. Discussion

The stages prior to the population monitoring (see Figure 2) are resource demanding. However, monitoring of a population is also a costly affair. Therefore, planning of the monitoring is important. In our paper we have outlined the principles for monitoring a population of employees from the occupational environment. We have emphasised that the monitoring should not be started unless most of the "black spots" in the population have been eliminated. It has been pointed out that in the general case the TWA defined on the individual employees is a random variable. The distribution of this variable cannot be considered as known. However, when the distribution is unimodal a generalised beta distribution may be used as an approximation for the

distribution (equation (1)). The distribution of the TWA value, X, for a randomly selected employee is a compound distribution of the individual distributions. We have only discussed the distribution of X in the case where the selection of employees has been random (equation (5) – (8)). In general the compound distribution will not be a standard distribution. However, when the collection of individual distributions is not too inhomogeneous, an approximation to the lognormal distribution may be acceptable (see Table 1). This situation could be expected when the criteria for starting the monitoring have been satisfied (see Figure 1a and b). In the paper it has been assumed that the observations are log normal distributed.

In our paper we have primarily outlined the case where the purpose with the monitoring is to secure that only a small fraction, p, of the employees in the population occasionally have TWA values exceeding the limiting value. Further we have treated the cases where the mean value and the median of the individual TWA values in the population should not exceed a fraction of the limiting value i.e. should not exceed the limit of concern (LOC) for E(X) and for the median. Relations between the three criteria have been calculated (see equation (15) – (16) and Figure 3). It is shown that the satisfaction of a criterion for the median does not give any general information whether a criterion for p is satisfied and vice versa. However, we have shown that for some combinations of the parameters the criterion for p is satisfied when the criterion for E(X) is satisfied.

Tests have been defined for testing whether for the probability, p, exceeds the LOC or does not (equation (18a and b). Correspondingly tests have been defined for testing whether E(X) exceeds the LOC or not (equation (23a and b). The test for demonstrating whether the median exceeds the LOC or not (see equation (17)) is a well known and is therefore not discussed in the paper. In order to test the criteria for p we have used a test analogous to a test given by Lehman (1959) (equation (21)). In Appendix instructions are given for calculation of the power for this test. A confidence interval for p can be used as an alternative test statistic. We have described how a confidence interval for p can be calculated. Since the likelihood test for testing the criteria for E(X) is complicated we have based the test on an approximate confidence interval for $\ln\{E(X/LV)\}$; (equation(20)). However, unfortunately the power of the test is based on the joint distribution of (S, $\overline{Z}$) and is therefore complicated to calculate.

7. Example

Consider a population of employees, which is monitored for a volatile hazardous compound. The limiting value for the individual TWA values is 9 mg/m^3. The LOC value for the mean in the

compound distribution characterising the population is chosen as $c_1LV = 0.20 \times 9$ mg/m^3 = 1.8 mg/m^3 (see equation (13)). The LOC for the value of p_0 is calculated from equation (10). It is recommended that 0.10 should be the maximum value for an employee having a TWA value exceeding LV. Further the relative number of employees in the population having a positive probability for their TWA value exceeding LV is recommended not to exceed 0.15. Thus, $p_0 = 0.15 \times 0.1 = 0.015$ and $e^{-\frac{1}{2}u^2_{1-p_0}} = 0.0949$. As $c_1 > 0.0949$, the line given in equation (12) intersects the parabola given in equation (14); see Figure 3. The set of admissible values of (τ, θ) for the criteria $E(X) \leq c_1LV$ is therefore not included in the set of admissible values of (τ, θ) for the criteria $p \leq p_0$. It is therefore necessary to perform tests for both the requirements. A sample of 15 employees was randomly selected from the population and the individual values of TWA measured. The measurement results are given as sample b in Table 1. The result of applying the transformation $Z = \ln Y = \ln(X/LV)$ on the observations is also given in Table 1.

The observed values for $\overline{Z}$, S^2 and T, respectively, are $\overline{Z}_{obs} - 0.731$, $S_{obs}^2 = (0.569)^2$ and $T_{obs} = -4.976$ (see equation (20) and (21)).

It should be noted that $(S_{obs}, \overline{Z}_{obs})$ are outside the sets of admissible values for the requirements given in equation (11) and (13); see Figure 3.

The non-centrality parameter in the distribution of T is $\eta = -8.40476$. The 0.05 and the 0.95 quantiles in the distribution of T are $t(14, -8.40476)_{0.05} = -12.7795$ and $t(14, -8.40476)_{0.95} = -6.0015$, respectively. As $T_{obs} > t(14, -8.40476)_{0.05}$ H_{10} cannot be rejected (see equation (16a)). The requirements for p can therefore not be stated as satisfied.

However, as $T_{obs} > t(14, -8.40476)_{0.95}$ H_{10}^* is rejected instead. Therefore, the requirements for p can thus be stated as not satisfied. The power functions for the two tests can be calculated from equation (A1) and (A2), respectively.

A $(1 - \alpha)$ confidence interval for p is calculated using equation (22a and b). For $\alpha = 0.05$ we obtain: $[p_L; p_H] = [0.025; 0.280]$. See Figure 4.

The estimated value of E(X) is $\hat{E}(X) = 5.05585$. The estimated value of $\ln(\hat{E}(Y))$ is thus $(\ln(\hat{E}(X)) - \ln(LV)) = -0.576678$.

A $(1 - 2\alpha)$ confidence interval for $\ln\{E(Y)\}$ is calculated from equation (24). For $\alpha = 0.05$ we obtain: $\{\ln(E_L); \ln(E_H)\} = (-0.830453; -0.307333)$.

As $\ln(E_L) > \ln(c_1) = -1.60944$, H_{20}^* is rejected i.e. beyond reasonable doubt it can be stated that the $E(X) > c_1LV = 1.8$ mg/m^3.

Appendix

The power of test for the probability of exceeding LV

The alternative hypotheses in equation (18a and b) can be expressed as H_{11}: $p = kp_0$ $(0 < k \leq 1)$ and H_{11}^*: $p = kp_0$ $(k > 1)$, respectively. The power function for both tests is thus a function of k. The power functions for the two tests are therefore respectively

$$\pi(k) = P\{T < t(n-1, \eta_0)_\alpha ; k\} \quad \text{(A1)}$$

and

$$\pi(k)^* = P\{T > t(n-1, \eta_0)_{1-\alpha} ; k\} \quad \text{(A2)}$$

As $T \in t(n-1, \eta = -u_{1-p}\sqrt{n})$ the power of the tests is easily calculated from equation (A1) and (A2).

List of notation

a, b	Respectively minimum and maximum value for X.
a_i, b_i	Respectively minimum and maximum value for X_i.
c_1, c_2	Factors used to express the requirements for E(X) and the median of X, respectively.
E(X), μ	Mean value of X.
E_L, E_H	Respectively the lower and the higher confidence limit for E(Y).
$f_i(x)$	The density function of X_i.
$F_i(x)$	The distribution function of X_i.
g(x)	The density function of X.
LOC	Limit of concern.
LV	Limiting value
N	Number of employees in Ω.
N_1	Number of employees in Ω with positive probabilities of exceeding LV.
p	The probability of TWA exceeding LV for a randomly selected employee in Ω i.e. $P(X > LV) = p$.
p_i	The probability of employee No. i having a TWA value exceeding LV
p_0	The LOC value for p.
p_L, p_H	Respectively the lower and the higher confidence limit for p.
r_i, s_i	Parameters in the distribution of X_i.
S^2	The empiric variance of the transformed TWA values in a random sample from Ω.
T, T_{obs}	The test statistic for testing the requirement for p and the observed value of T, respectively.
TWA	Time weighted average concentration
Var(X), σ^2	The variance of X.
W_t	Number of employees in Ω at time t with TWA values exceeding LV.
X	The TWA value of a randomly selected employee from Ω.

X_i	The TWA value of employee No. i in Ω.
Y	X/LV
Z	ln(Y)
Z_i	The transformed TWA value for employee No. i in a random sample from Ω.
$\bar{Z}$	The arithmetic mean of the transformed TWA values in a random sample from Ω.
α	The level of significance for the tests performed.
$\Gamma(\cdot)$	The gamma function.
η	The non-centrality parameter in the distribution of T.
η_0	The non-centrality parameter in the distribution of T when $p = p_0$.
θ	Mean of Z and ln(Y) i.e. $E(Z) = E\{\ln(Y)\}$.
θ_X	Mean of ln(X) i.e. $E\{\ln(X)\}$.
μ_0	The LOC value for E(X).
μ_p	The mean of all the individual p values for the employees in Ω.
σ_B^2	The variance between the entire individual TWA means of the employees in Ω.
σ_p	The variance between all of the individual p values for the employees in Ω.
σ_W^2	The weighted mean of all the individual TWA variances within employees in Ω.
τ	Standard deviation of ln(X) and ln(Y).
υ_L, υ_H	Respectively the smallest and the largest positive value of p for the employees in Ω.
Ω	The population of employees exposed to a volatile hazardous compound.

Table 1. Measurement results from two samples selected from a population of employees (simulated data). Sample A was selected before the population was ready for monitoring while sample B was selected after the monitoring was started (see Figure 2a and b). Both samples were transformed using the transformation Z = ln(X/LV). The hypothesis of normal distribution for the transformed samples was tested using the Anderson-Darling test. The observed levels of significance were 0.09 for sample A and 0.12 for sample B.

Sample A	Sample B	Sample A transformed	Sample B transformed
6.4406	2.1932	-0.33460	-1.41186
2.6257	2.4837	-1.23188	-1.28748
9.6978	10.9811	0.07468	0.19895
11.3854	9.7667	0.23511	0.08175
9.7084	2.7924	0.07577	-1.17033
13.2401	6.9307	0.38603	-0.26127
10.6537	3.6668	0.16868	-0.89789
8.4175	3.1004	-0.06691	-1.06570
3.1862	1.9739	-1.03839	-1.51722
1.6722	3.2288	-1.68309	-1.02511
7.6188	7.6023	-0.16661	-0.16878
8.6059	6.0103	-0.04477	-0.40375
4.0436	3.4905	-0.80008	-0.94719
6.3989	8.3168	-0.34109	-0.07895
2.9966	3.3002	-1.09976	-1.00325

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Text for figures

Fig. 1a. Probability density functions for the value of the TWA for 15 employees in a random sample from a population of employees exposed to a hazardous volatile compound. The distributions were chosen as beta distributions (assessed from a monitoring programme), and the sample was obtained as a simulated sample from these distributions. The individual observations are given in Table 1 together with the result of a goodness of fit test for the lognormal distribution. The limiting value for the TWA is in this case 9 mg/m^3. The sample illustrates that the population can be assumed to include a number of employees with large probabilities of exceeding the limiting value. The population should therefore be monitored at the individual level in order to eliminate the "black spots".

Fig. 1b. Probability density functions for the value of the TWA for 15 employees in a new random sample from the population referred to in Figure 1a. The individual observations are given in table 1 together with the result of a goodness of fit test for the lognormal distribution. The sample is selected after some time of individual monitoring and the elimination of a number of "black spots". It is obvious that the number of employees in the population with large probabilities of exceeding the limiting value is reduced. Therefore, it should be evaluated whether a population monitoring should be started.

Fig. 2. The flow diagram displays the initiatives established before a population of employees from the occupational environment should be monitored. The first step in the monitoring program is often a mapping of the population of the employees of interest (Seedorf and Olsen, 1990). The mapping should give some information on the distribution of the value of the TWA in the population. The selection of the locations for further measurement will commonly be highly biased towards employees with known unsatisfactory values of the TWA. This is desirable as one of the purposes of the occupational health system is to locate and eliminate the "black spots" of the working environment. When this can be assumed to be the case it is decided whether monitoring of the individual employees in the population should be started. After the monitoring is started, intervention and assessment of the intervention normally follow.

Fig. 3. Admissible values of (θ, τ) for the requirement $P(X > LV) = P(Y > 1) \leq p_0$. It is assumed that the distribution for Y is log normal (i.e. $Y \in LN(\theta, \tau^2)$). The admissible values are located in the fourth quadrant below the line $\theta = -u_{1-p_0}$ where u_{1-p_0} is the $(1 - p_0)$ quantile in the standard

normal distribution. For the requirement $E(Y) \leq c_1$ the admissible values of (θ, τ) are located in the fourth quadrant below the parabola $\theta = -\tau^2/2 + \ln(c_1)$ where $c_1 = 0.20$. The figure displays the situation where $p_0 = 0.015$ and the line intersects the parabola. (see equation (15) and the example). When there exist a requirement for the median of X e.g. $e^{\theta_x} \leq c_2 LV$ where $0 < c_2 \leq 1$ then the admissible values of (θ, τ) are located in the fourth quadrant below the line $\theta = \ln(c_2)$. The situation is illustrated for $c_2 = 0.20$.

Fig. 4. The principle construction of a two-sided $(1 - \alpha)$ confidence interval for $p = P(X > LV)$. The probability $P[T \leq T_{obs}; T \in t\{(n-1), -u_{1-p}\sqrt{n}\}] = h(p)$ is a function of p. The functional value of the lower confidence limit, p_L, of the confidence interval is $(1 - \alpha/2)$ i.e. $h(p_L) = 1 - \alpha/2$. For the higher confidence limit, p_H, we have $h(p_H) = \alpha/2$. In the figure $T_{obs} = -4.976$ (see the example).

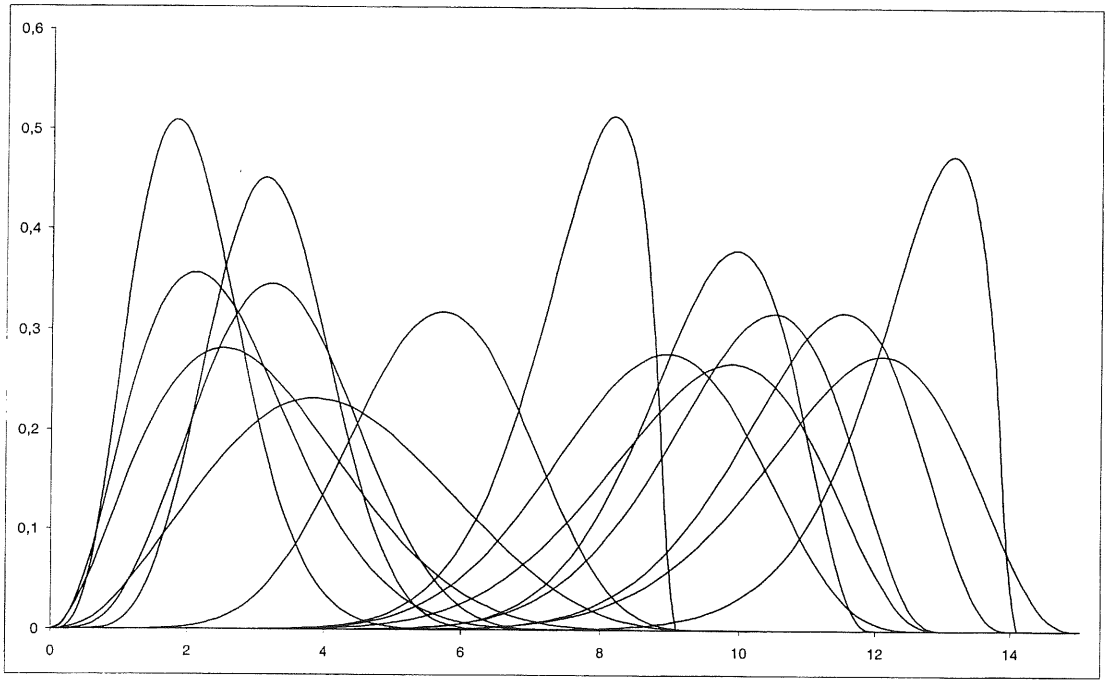
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Fig. 1a

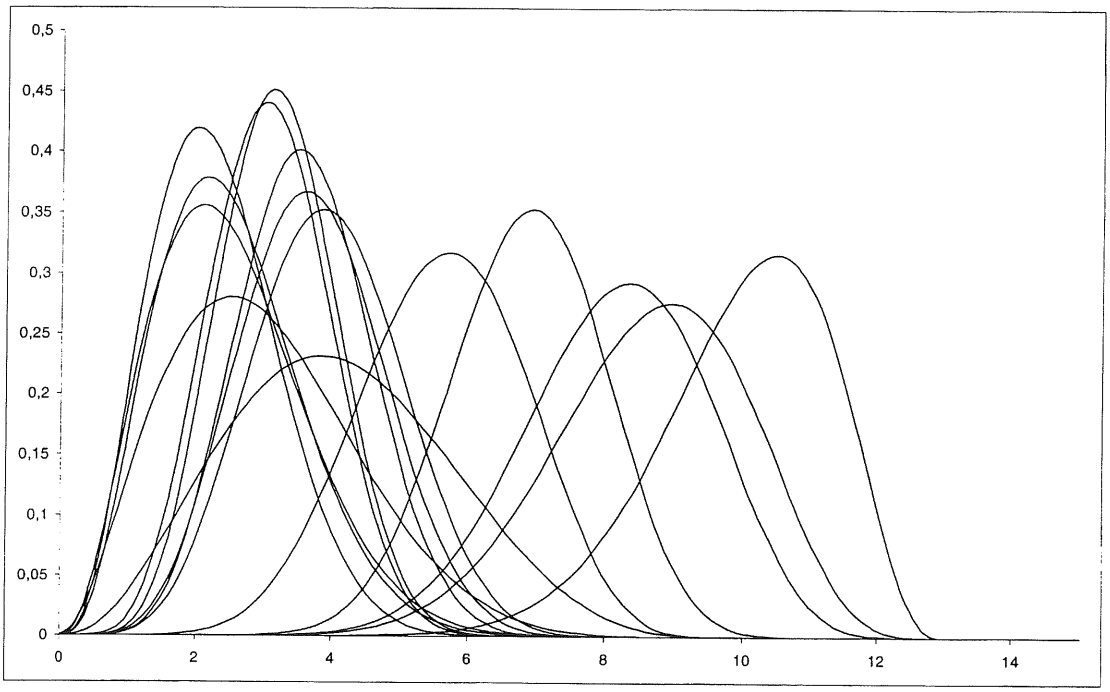
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Fig. 1b

BRINGING EXPOSURE UNDER CONTROL

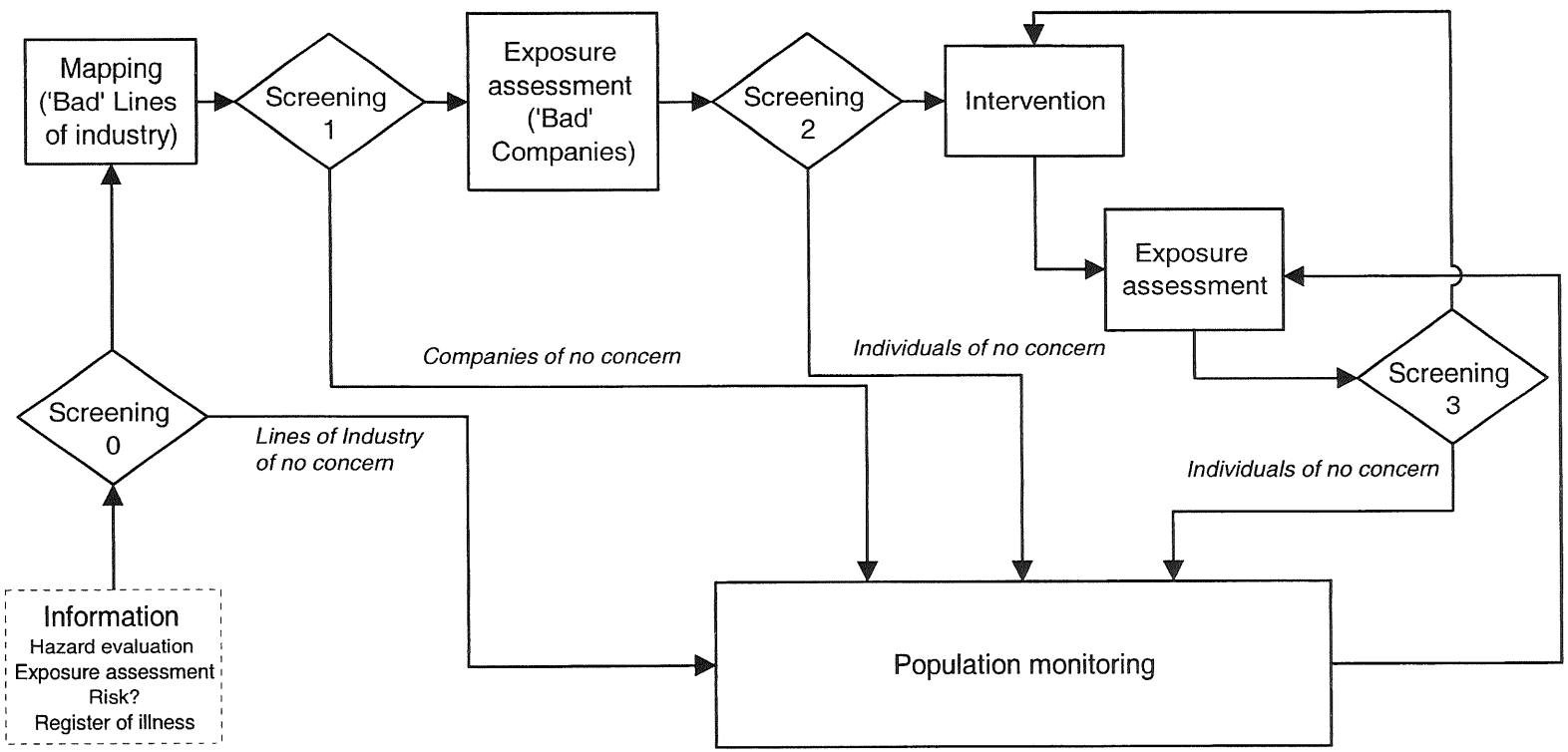


Fig. 2

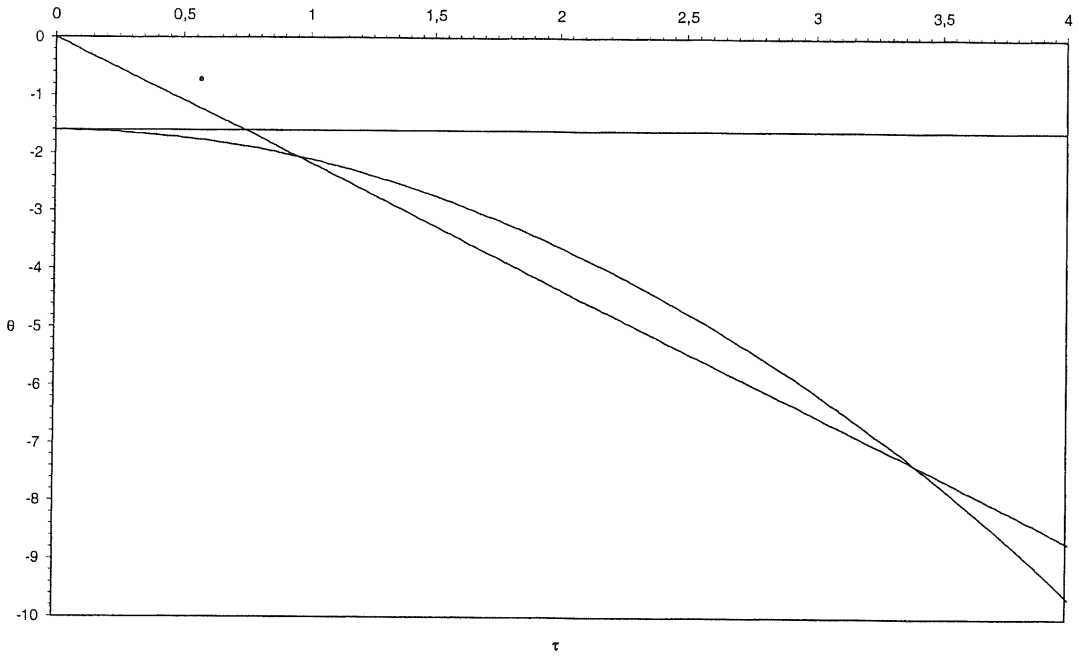
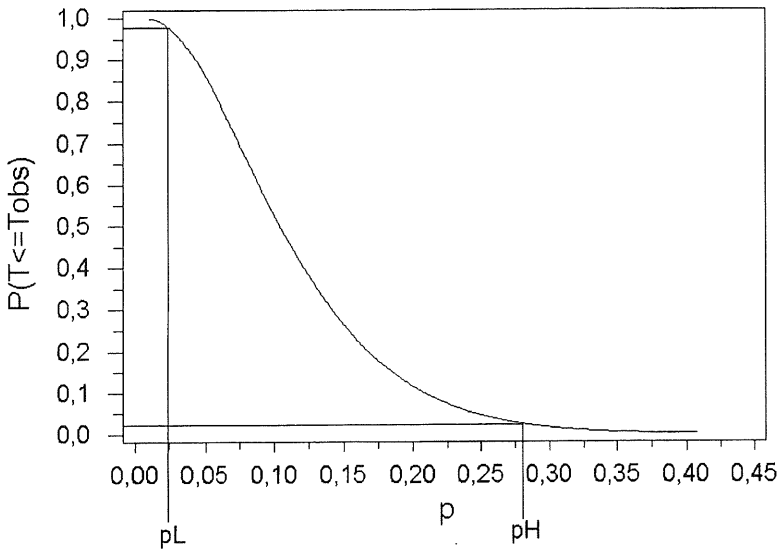


Fig. 3


P(T<=Tobs)
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0,8
0,7
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0,1
0,0
0,00
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0,10
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0,45
p
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pH

Fig. 4